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MANHATTAN PROJECT TECHNICAL SERIES

THE CHEMISTRY OF URANIUM (I)

by

E.I. RABINOWITCH AND J.J. KATZ

AEC RESEARCH AND DEVELOPMENT REPORT

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CONTENTS

PART I

THE ELEMENT URANIUM

Chapter 1

THE NUCLEAR PROPERTIES OF URANIUM

Chapter 2

PROPERTIES OF THE URANIUM ATOM

Chapter 3

URANIUM IN NATURE

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CONFIDENTIAL

DECLASSIFIED

CONFIDENTIAL

P8

CHAPTER 11

PART I URANIUM OXIDES AND HYDROXIDES

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H. R. C
Chief, Declassification Branch

DECLASSIFIED

CONFIDENTIAL

p. 62

CONFIDENTIAL

DECLASSIFIED

CHAPTER 11

PART I URANIUM OXIDES AND HYDROXIDES

Introduction

The three oxides UO_2, U_3O_8 and UO_3 have been known for over a hundred years, but a systematic investigation of the uranium-oxygen system was first undertaken by Hüttig, Biltz and co-workers in 1920-1928. Recent studies at the Manhattan Project and in Britain have provided considerable new information, including the discovery of uranium monoxide, UO.*

The solubility of oxygen in uranium is small and the same is true of the solubility of uranium in uranium monoxide; in other words, the range U to UO is essentially diphasic. This was also considered to be true of the range UO to UO_2 until Zachariasen found in 1946 a homogeneous phase with the composition $UO_{1.75}$. This may be either a new compound (U_4O_7), or the lower end of a series of solid solutions which previously was known to extend from $UO_{2.00}$ to $UO_{2.30}$. Above $UO_{2.30}$ there follows a diphasic region, the upper limit of which is not definitely established. The existence of an oxide $UO_{2.5}$

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* A systematic study of the U/O system also was promised in a note from E. Gleditsch's laboratory at Oslo (Nature, 28, 127 (1940)), but the results of this study, if any, were not available at the time of the writing of this review.

(U_2O_5) was asserted several times in the earlier literature and, recently, at Ames a homogeneous phase with this composition again was found by x-ray analysis. According to Ames observers, $UO_{2.5}$ is the lower end of a monophasic region which extends up to and beyond $UO_{2.67}$ ($\equiv U_3O_8$). On the other hand, Biltz and Müller's tensimetric analysis of the uranium-oxygen system gave no indication of the existence of a compound U_2O_5. According to their observations, the lower limit of existence of a third homogeneous uranium-oxygen phase (after UO and UO_2) is at $UO_{2.62}$ quite close to $UO_{2.67}$ (U_3O_8). While it is thus uncertain whether the monophasic range begins at $UO_{2.50}$ or at $UO_{2.62}$, there is no doubt that the upper limit of this homogeneous range extends far beyond $UO_{2.67}$ - in all probability/ up to UO_3.

The phases UO and UO_2 (more exactly, $UO_{1.75}$ to $UO_{2.30}$) are cubic face-centered; the first one has the rock salt structure, the second the fluorite structure. The phases between $UO_{2.50}$ (or $UO_{2.62}$) and $UO_{3.00}$ show a continuous transition from an orthorhombic to an hexagonal lattice. In addition to the hexagonal form, UO_3(I), uranium trioxide also exists in one amorphous, and in at least two, and perhaps four, other (as yet unidentified) crystalline forms.

The affinity for water increases from UO_2 to UO_3. The hydrates $UO_2 \cdot xH_2O$ and $U_3O_8 \cdot xH_2O$ (with x probably equal to 2) are known, but have not been very well investigated. Several UO_3-hydrates, on the other hand, have been well identified, both crystallographically and analytically. They include the semi-hydrate $2UO_3 \cdot H_2O$ ($=H_2U_2O_7$), four allotropic forms of the monohydrate $UO_3 \cdot H_2O$ ($=H_2UO_4$) and two allotropic forms of the dihydrate $UO_3 \cdot 2H_2O$ ($=H_4UO_5$).

The oxide UO_2 is strongly basic. The oxide UO_3 is amphoteric, i.e. it can be neutralized either by acids, forming uranyl salts (e.g. UO_2SO_4) or by alkalis, forming uranates (e.g. Na_2UO_4). The oxide U_3O_8 has often been interpreted as urano-uranate, $UO_2 \cdot 2UO_3$, or $U^{+4}(UO_4^{-2})_2$. In agreement with this concept, U_3O_8 gives with acids mixtures of uranium (IV) and uranyl salts. However, the formula $UO_2 \cdot 2UO_3$ should not be taken as indicating the presence in U_3O_8 of two types of uranium atoms. X-ray analysis shows that all uranium atoms in U_3O_8 occupy equivalent positions; they thus probably carry also the same average charge (+ 5 1/3). This fractional charge can be maintained by resonance between two (or more) valence states (e.g. U^{4+} and U^{6+}).

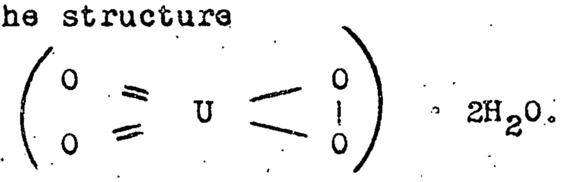
Magnetic investigations (cf. p.40) have been interpreted to show that U_3O_8 contains U^{5+} ions rather than U^{4+} ions and it was suggested that the formula of this compound should be written $U_2O_5 \cdot UO_3$ rather than $UO_2 \cdot 2UO_3$. However, here again, the interpretation must take into account the existence of mesomerism. In other words, U_3O_8 must be described as a mesomeric compound that behaves in the presence of acids as if it contained the ions U^{4+} and U^{6+}, and in a magnetic field as if it contained the ions U^{5+} and U^{6+}.

The nature of oxides with more than three oxygen atoms per uranium atom is not completely understood. Anhydrous oxides with $O:U = 3.2 - 3.5$ have been obtained by dehydration of $UO_4 \cdot 2H_2O$, or decomposition of ammonium diuranate in a stream of oxygen (cf. p. 119); and allegedly also by electrolysis (cf. p. 53). These oxides decompose to UO_3 and oxygen in contact with water, and to UO_2^{++} salts and oxygen in contact with acids. The Brown University Group considered $UO_{3.5}$ as an equimolar mixture of UO_3 and anhydrous uranium tetroxide UO_4; however, it is not clear why $UO_{3.5}$ should not be tentatively considered as a separate oxide, U_2O_7, since all attempts to prepare pure anhydrous UO_4 have so far been unsuccessful (cf. p. 62).

Hydrated UO_4 may contain, in the air-dry state, up to 4.5 moles H_2O; according to most observers, however, the only definite UO_4 hydrate is $UO_4 \cdot 2H_2O$. In contrast to anhydrous $UO_{3.5}$, the hydrate $UO_4 \cdot 2H_2O$ is not decomposed by water or acids; in 4 N H_2SO_4 it gives a weak solution capable of reducing $KMnO_4$. Consequently, $UO_4 \cdot 2H_2O$ should perhaps be considered as free "peruranic acid" H_4UO_6 (i.e. $UO(OH)_3(OOH)$) giving, in equilibrium with water, a small amount of H_2O_2:

$$(1) \qquad \underset{\text{(peruranic acid)}}{UO(OH)_3(OOH)} + H_2O \rightleftharpoons H_2O_2 + \underset{\text{(uranic acid)}}{UO(OH)_4}$$

The interpretation of $UO_4 \cdot 2H_2O$ as free peruranic acid was first suggested long ago by Fairley (1877) and Pissarjevsky (1903), but was opposed by Rosenheim and Daehr (1932), who pointed out that $UO_4 \cdot 2H_2O$ cannot be neutralized by alkalis to form perurantes. They determined the "peroxide" oxygen in $UO_4 \cdot 2H_2O$ by titration with permanganate or iodine according to the method of Riesenfeld and Mau (1911), and found one oxygen atom to be "peroxidic." On the strength of this result they suggested the structure



$$\left(\begin{array}{c} O \\ O \end{array} \begin{array}{c} = \\ = \end{array} U < \begin{array}{c} O \\ | \\ O \end{array}\right) \cdot 2H_2O.$$

Hüttig and v. Schroeder (1922), on the other hand, formulated the uranium peroxide hydrates as addition compounds of UO_3 and H_2O_2:

$(UO_3) \cdot xH_2O_2 \cdot yH_2O$ $(x = 1, y = 1 \text{ for } UO_4 \cdot 2H_2O)$

All these suggestions carry little weight and a significant description of the constitution of $UO_4 \cdot 2H_2O$ can be based only on a complete x-ray analysis, which has not as yet been carried out.

1. Phase Relationships in the Uranium-Oxygen System.

1.1 Range U-UO; the Solubility of Oxygen in Uranium; the Uranium Monoxide.

1.2 Range UO-$UO_{2.30}$; the Uranium Dioxide.

1.3 Range $UO_{2.30}$-$UO_{2.67}$; the Oxides U_2O_5 (?) and U_3O_8.

1.4 Range $UO_{2.67}$-UO_3; the Uranium Trioxide.

1.5 Range above UO_3; the Oxides U_2O_7 (?) and UO_4.

1. Phase Relationships in the System Uranium-Oxygen

1.1 **Range U to UO; Solubility of Oxygen in Uranium; the Uranium Monoxide.** The solubility of oxygen in uranium is very small, even at temperatures above 2000°C. The best available results, obtained at the National Bureau of Standards (Nat. Bur. Standards 1,2), are plotted in Fig. 1. The curve shows a solubility of the order of 0.05 atom per cent oxygen at the melting point of uranium (1132°C) rising to 0.1 per cent at 1400°C and 0.4 atom per cent at 2000°C. The solubility of oxygen (or uranium oxide) in solid uranium could not be determined exactly, but the fact that oxide inclusions appear (after annealing in the γ-range) even in metal containing as little as 0.05 atom per cent oxygen, shows that solubility in the solid phase is even smaller than in the liquid. This is indicated by the dotted line in Fig. 1.

According to the National Bureau of Standards (Nat. Bur. Standards 3), uranium oxides precipitate from oxygen solutions in molten uranium upon cooling; precipitation occurs in either the β or the γ-range, depending on the original oxygen concentration.

At Ames (MP Ames 1) uranium oxide samples of varying composition were prepared by heating compressed mixtures of uranium metal powder and uranium dioxide in vacuo. In the composition range x = 0 to 1, the products gave only uranium and uranium monoxide x-ray diffraction patterns. The lattice spacing of α-uranium was not markedly affected by the presence

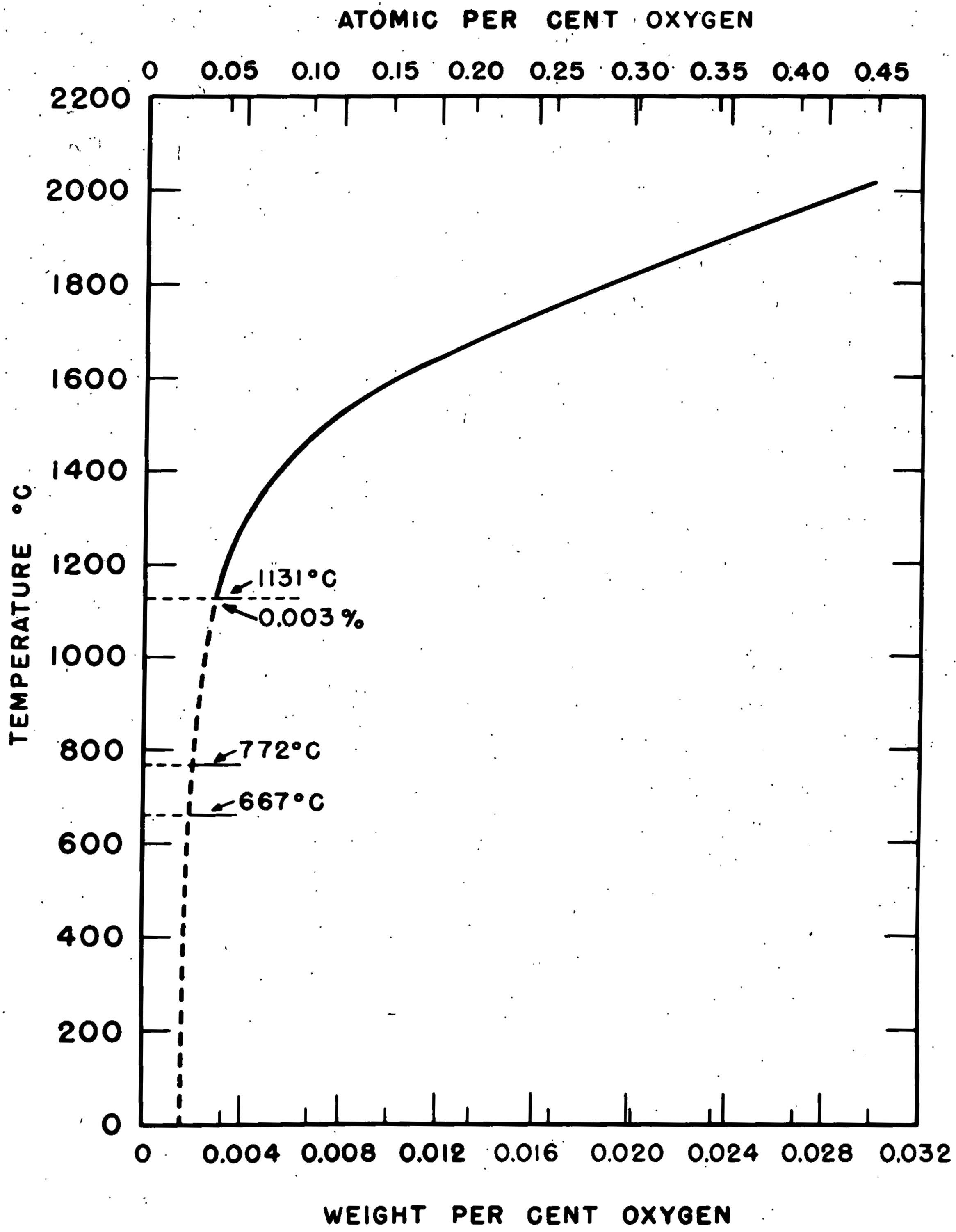


FIG. I. SOLUBILITY OF OXYGEN IN URANIUM.

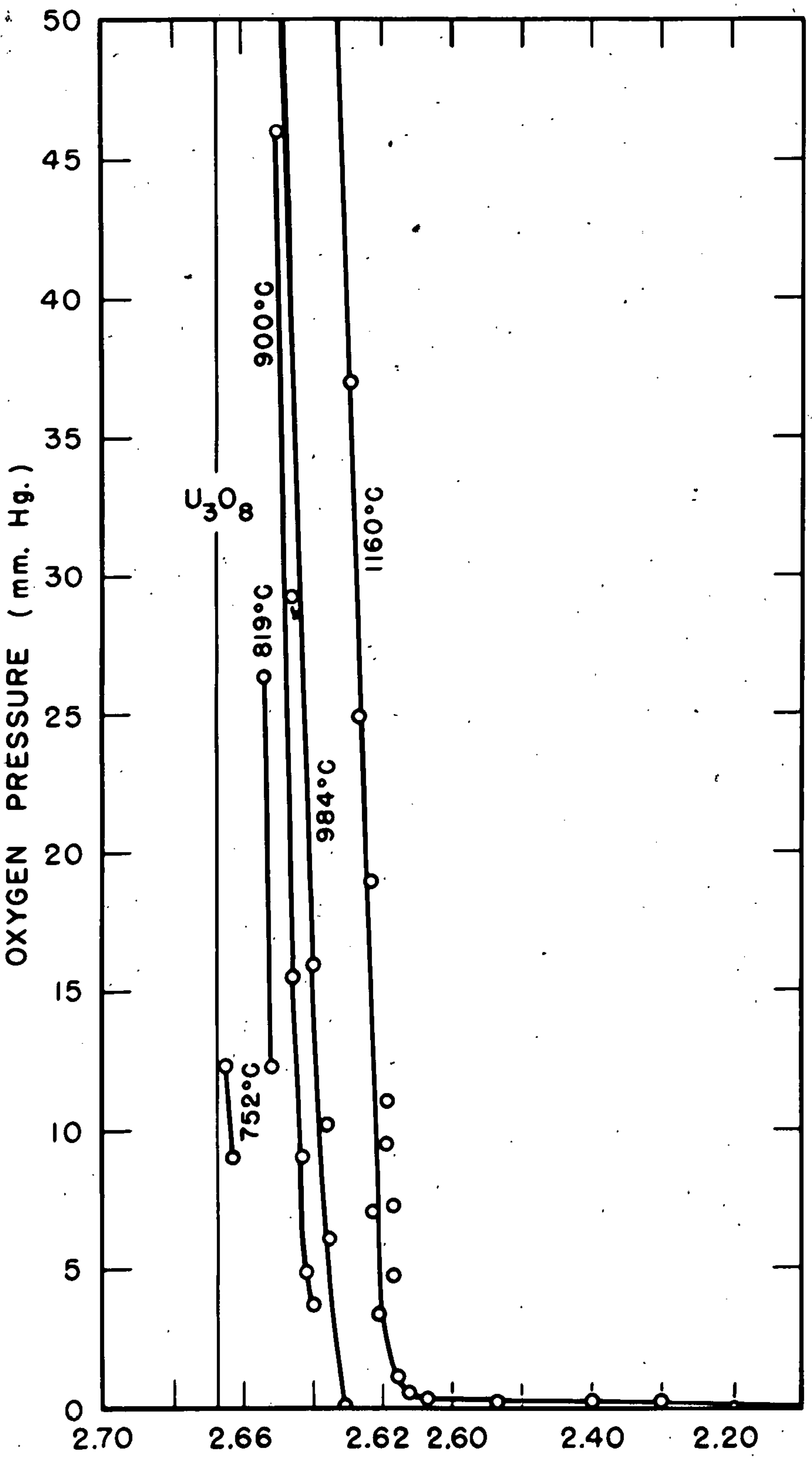


FIG. 2. DECOMPOSITION ISOTHERMS OF $UO_{2.665}$ TO $UO_{2.200}$. (FROM W. BILTZ AND H. MÜLLER, Z. ANORG. ALLGEM. CHEM., <u>163</u>, 279 (1927)).

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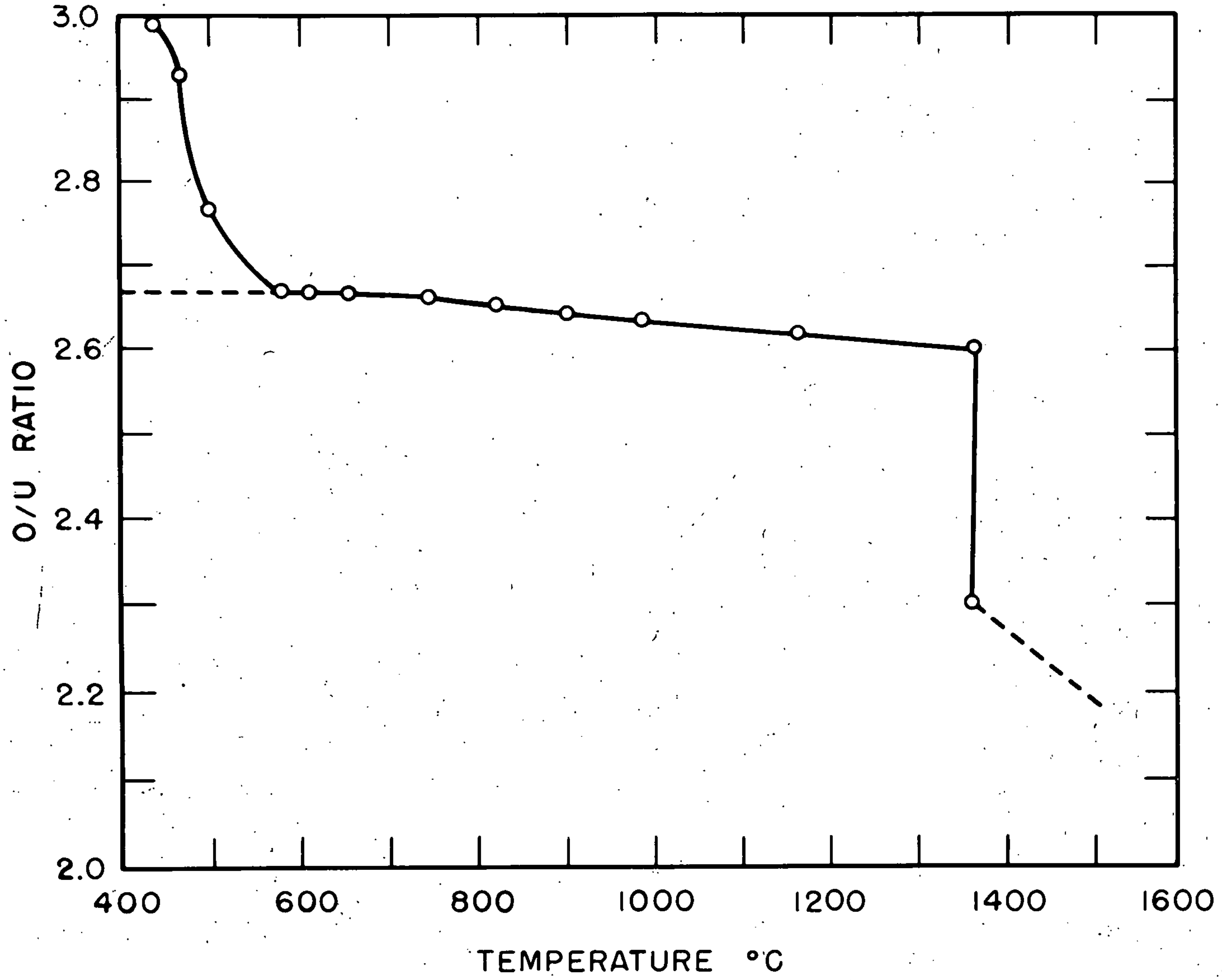

FIG. 3. THE CHANGE IN URANIUM-OXYGEN COMPOSITION WITH TEMPERATURE AT A CONSTANT OXYGEN PRESSURE OF 10 mm. Hg. (FROM W. BILTZ AND H. MÜLLER, Z. ANORG. ALLGEM. CHEM., 163, 295 (1927)).

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Biltz and Müller (1927) saw in cleveite a mineral with the UO_2 structure but with a composition close to U_3O_8 and consequently suggested that the UO_2 phase can take up even more oxygen than corresponds to the formula $UO_{2.30}$; but this interpretation of cleveite structure is probably incorrect (cf. chapter 3).

There is disagreement as to the extent of the homogeneous portion of the range UO to $UO_{2.30}$. According to Ames x-ray observations, the region extending from UO to close to $UO_{2.00}$ is diphasic. Only a very limited solubility of UO in UO_2 is indicated by the slight change in the UO_2 lattice constant produced by heating UO_2 with uranium metal powder ($a_0 \cong 5.461$A for $UO_2 + U$ as against $a_0 \cong 5.459$A for pure UO_2, cf. Table 3).

On the other hand, Zachariasen (MP Chicago 1) found a homogeneous space-centered cubic phase with a composition of approximately $UO_{1.75}$ ($\cong U_4O_7$, tetrauranium heptoxide). Since this phase was present at the same time as the normal UO_2 phase (also face-centered cubic, but with a smaller spacing), U_4O_7 may be a separate compound, analogous to Th_4S_7. However, this conclusion is not quite certain. Occasionally, two phases, similar in crystal structure but different in composition, have also been observed in the undoubtedly monophasic range between $UO_{2.00}$ and $UO_{2.30}$ where their presence must have been due to incomplete equilibration. It is therefore possible (MP Berkeley 1) that the solid solution range now being discussed extends down to $UO_{1.75}$, and that the simultaneous occurrence of $UO_{1.75}$ with $UO_{2.00}$ also was due to a lack of equilibrium. This hypothesis is supported by x-ray analysis. All oxides between $UO_{1.75}$ and $UO_{2.3}$ crystallize with the cubic, face-centered fluorite structure. According to Table 3, the lattice constant of $UO_{1.75}$ is 5.477A, that of stoichiometrically pure UO_2 is 5.460A, and that of $UO_{2.30}$ is 5.430A; this uniform change of spacing makes the hypothesis of a continuous series of solid solutions plausible. It is noteworthy that the lattice constant decreases with increasing oxygen content. This shrinkage led Rundle and co-workers at Ames to advance the suggestion that the increase in the O:U ratio may be due to deficiency of uranium, rather than to presence of extra oxygen. If this hypothesis is correct, the density of the oxides should decrease considerably from $UO_{2.00}$ (or $UO_{1.75}$) to $UO_{2.30}$. On the other hand, Hüttig (1924) suggested that oxygen atoms in excess of the formula UO_2 may be freely movable in the UO_2 crystal lattice; Biltz and Müller (1927) assumed that they are held in the "interstitial" spaces of the UO_2 lattice. According to these concepts, the density of $UO_{2.30}$ should be higher than that of UO_2, since the unit cell of $UO_{2.30}$ must contain, despite its somewhat smaller size, the same number of uranium atoms and 15 per cent more oxygen atoms than the unit cell of $UO_{2.00}$.

The experimental data on the density of uranium oxides between $UO_{2.00}$ and $UO_{3.00}$ are given in Table 1. They show, in the first place, that the empirical density of $UO_{2.00}$ agrees well with the value calculated from the x-ray diffraction data on the assumption that each elementary cell contains its full complement of four uranium atoms. In the second place, the experimental densities increase slightly from $UO_{2.00}$ to $UO_{2.30}$. This proves that no substantial fraction of uranium is "missing" either in $UO_{2.00}$ or in the higher oxides up to $UO_{2.30}$ (about a probable small deficiency of uranium, too small to affect density determinations but enough to account for electrical conductivity, see p. 38).

The observed increase in density between $UO_{2.00}$ and $UO_{2.30}$ is somewhat less pronounced than would be expected from the x-ray data on the assumption of no "deficit" of uranium or oxygen (cf. last column of Table 1). The mole volumes, calculated by Biltz and Müller (column five of this Table), are practically constant from $UO_{2.0}$ to $UO_{2.26}$, while the lattice constants require that these volumes should decrease by about 1.7 per cent. However, the density measurements may have been not accurate enough to reveal the anticipated decrease.

TABLE 1

DENSITIES OF UO_x

x	ρ g/cc		Mole Volume cc/mole		Oxygen volume cc/g atom Biltz*	ρ g/cc calculated from x-ray data
	Hillebrand (1893)	Biltz and Müller (1927)	Hillebrand (1893)	Biltz and Müller (1927)		
1.992	--	10.80	--	25.03	6.2	--
2.000	--	10.87	--	25.09	6.2	10.97
2.005	10.95	--	24.69	--	--	11.15
2.015	10.88	--	24.85	--	--	
2.018	--	10.71	--	25.25	6.2	11.22
2.022	10.82	10.82	25.01	25.01	6.1	
2.028	10.86	--	24.92	--	--	--
2.051	10.83	--	25.02	--	--	--
2.078	--	10.72	--	25.31	6.1	--
2.098	--	10.94	--	24.89	5.7	--
2.132	10.89	--	25.00	--	--	--
2.152	--	10.62	--	25.58	6.0	--
2.162	--	11.08	--	24.62	5.5	--
2.193	--	10.87	--	25.14	5.7	--
2.200	--	10.87	--	25.15	5.7	--
2.201	10.98	--	24.90	--	--	--
2.207	--	10.94	--	25.00	5.6	--
2.262	--	10.90	--	25.17	5.5	11.35
2.306	--	10.40	--	26.44	5.9	
2.318	10.47	--	26.29	--	--	--
2.333	--	9.754	--	28.24	6.65	--
2.349	--	10.34	--	26.67	5.95	--
2.417	10.15	--	27.28	--	--	--
2.451	--	9.469	--	29.30	6.8	--
2.454	--	9.38	--	29.58	6.9	8.33**
2.537	--	8.773	--	31.77	7.5	
2.631	--	8.379	--	33.44	7.9	--
2.643	--	8.369	--	33.51	7.8	--
2.660	--	8.216	--	34.18	8.1	--
2.666	--	8.300	--	33.83	7.9	8.39
2.685	--	7.938	--	35.43	8.5	--
2.920	--	7.074	--	40.28	9.45	--
3.069	--	6.039	--	47.57	11.4	--

* Obtained by subtracting from the mole volume, 12.7 cc as the volume of the uranium atom, and dividing the residue by x.

** U_2O_5, according to p. 35.

1.3 The Range $UO_{2.30}$ to $UO_{2.67}$; the Compound U_3O_8. In this region, too, there is a disagreement between the conclusions reached at Ames from crystallographic measurements and the tensimetric data of Biltz and Müller. The disagreement concerns the composition of the orthorhombic phase, which is present (together with the cubic UO_2 phase) when x in UO_x exceeds 2.30.

According to the Ames x-ray analyses (MP Ames 2) this phase has the composition $UO_{2.50}$. A pure homogeneous phase of this composition was obtained at Ames by heating together equal quantities of UO_2 and U_3O_8. The crystal structure of the new phase was found to be somewhat different from that of U_3O_8 although both are orthorhombic; it may therefore be considered a separate compound, diuranium pentoxide, U_2O_5. Single, needle-shaped crystals exhibiting the x-ray pattern of U_2O_5 have been obtained accidentally at Ames (accompanied by octahedral $UO_{2.3}$ crystals) during an experiment in which UO_2Cl_2 was decomposed at 900°C. Despite the difference in crystal structure, U_2O_5 can be converted into U_3O_8 by gradual uptake of oxygen without the formation of a new phase.

The existence of a homogeneous phase U_2O_5 also was asserted by several earlier investigators, particularly Oechsner de Coninck (1901,1903), de Coninck and Camo (1901), de Coninck and Reynaud (1912) and Schwartz (1920); but denied by others, e.g. Lebeau (1922), Jolibois and Bossuet (1922) and, particularly, Biltz and Müller (1927a).

Biltz and Müller measured the pressures of oxygen over uranium oxides of various composition. Between $UO_{2.67}$ ($=U_3O_8$) and $UO_{2.20}$, decomposition pressures were established rapidly and reversibly, and therefore appear to be true equilibrium pressures. Because of the rapid change in oxygen pressure with composition, reliable p versus x curves can be obtained in this range only if the composition of the solid is determined exactly. This was done by Biltz and Müller, either by direct analysis or by calculation from the amount of oxygen in the gas phase. Earlier investigations of the decomposition pressure of uranium oxides, in which this point was neglected, are of little value, particularly those in which a relatively small amount of solid was used in a large volume of gas, as in the measurements of Schwartz (1920).

Fig. 2 shows four decomposition isothermals (752°C to 1160°C). It reveals a very rapid change of dissociation pressure with composition, particularly between $UO_{2.67}$ ($=U_3O_8$) and $UO_{2.62}$.

An interpretation of this decline was attempted by Wagner and Schottky (1931) on the basis of their theory of "ordered mixed phases." They attributed the change in decomposition pressure with decreasing oxygen content to an increased number of "holes" in the oxygen sublattice of U_3O_8. This theory leads to a linear relationship between $1/\sqrt{p_{(O_2)}}$ and the deviation from stoichiometric composition; such a relation is actually found in the 900°C and 984°C isotherms (but not in the 1160°C isotherm) in Fig. 4, in the region between $UO_{2.67}$ and $UO_{2.69}$.

The undoubtedly monophasic region between $UO_{2.67}$ and $UO_{2.62}$ is followed according to Biltz and Müller by a region of constant pressure which, according to the phase rule, must correspond to a diphasic system. This region extends from $UO_{2.61}$ to $UO_{2.30}$; no homogeneous phase with the composition $UO_{2.50}$ exists according to these measurements. The dissociation pressure begins to decline again with decreasing x only in the well known monophasic region below $UO_{2.30}$; this decline could be followed at

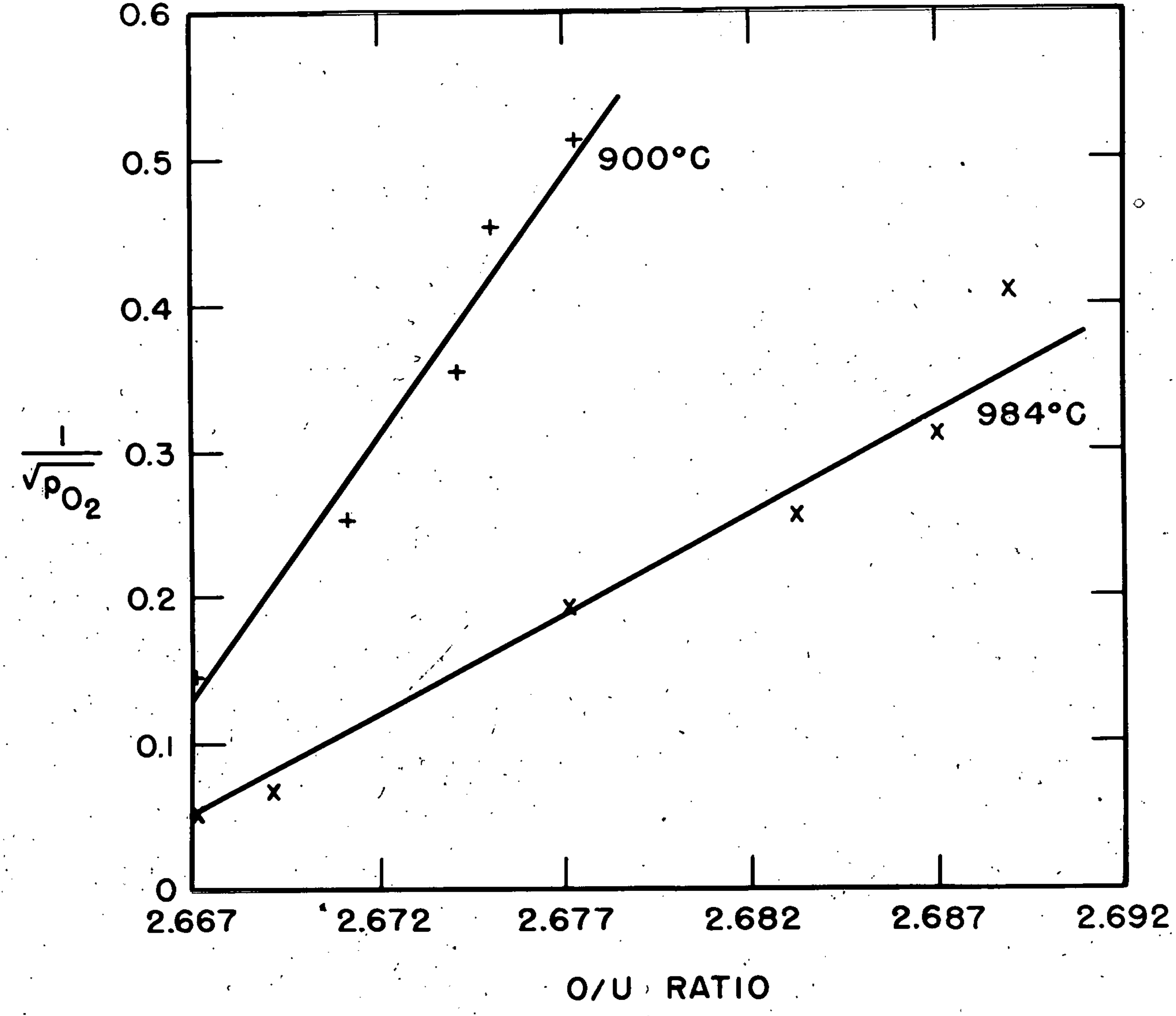

FIG. 4. CHANGE OF DISSOCIATION PRESSURE WITH URANIUM-OXYGEN RATIO. (FROM C. WAGNER AND W. SCHOTTKY, Z. PHYSIK. CHEM., (B), 11, 200 (1931)).

1160°C down to $UO_{2.20}$ where the pressure was 0.022 mm, the lowest value measured by Biltz and Müller. Further decomposition, leading to the conversion of $UO_{2.20}$ to $UO_{2.00}$, requires temperatures much higher than 1160°C.

The decomposition pressures of the oxides $UO_{2.26}$, $UO_{2.46}$ and $UO_{2.61}$ were found by Biltz and Müller to be identical not only at 1160°C but also at several higher temperatures up to 1240°C. From the observed or extrapolated pressure values, Biltz and Müller constructed a uranium-oxygen isobar corresponding to 10 mm oxygen pressure (Fig. 3). Under this pressure U_3O_8 is stable between 580°C and somewhere above 650°C. Between 750°C and 1360°C U_3O_8 loses oxygen gradually. The vertical segment of the isobar between $UO_{2.62}$ and $UO_{2.30}$ indicates a diphasic region. The last dotted part of the isobar shows the loss of oxygen by $UO_{2.30}$; as mentioned above, it could be followed only down to $UO_{2.20}$.

In pointing out the discrepancy between the tensimetric data of Biltz and Müller and the alleged existence of U_2O_5, Brewer (MP Berkeley 1) suggested that the Ames observation of a homogeneous orthorhombic U_2O_5 phase could perhaps be attributed to the fact (pointed out by Biltz and Müller) that the relatively simple, cubic UO_2 diffraction pattern is easily obscured by the more complex orthorhombic pattern of U_3O_8. As to the assertion that single U_2O_5 crystals have been obtained at Ames, Brewer pointed out that no chemical analysis of these crystals has been made. If, however, the Ames observations prove to be correct, then either Biltz and Müller's pressure measurements must be discarded as erroneous, or the lower limit of the monophasic range must be assumed to decline with falling temperature from $UO_{2.62}$ at 1160°C to $UO_{2.50}$ at room temperature, which is unlikely.

The crystal structure attributed to U_2O_5 by the Ames observers is described on p. 34 . It corresponds to a density of 8.33 g/cc. No such low density was observed in the region of $x = 2.5$ by Biltz and Müller (cf. Table 1), who found a practically linear decrease of δ with x from $x = 2.3$ to $x = 2.92$ (cf. Fig. 2).

The crystal structure of U_3O_8 is described on p. 35 ; it is orthorhombic and corresponds to a density of 8.39, in approximate agreement with the results of direct measurement shown in Table 1.

1.4 The Range $UO_{2.67}$ to $UO_{3.0}$; Uranium Trioxide. According to Biltz's tensimetric data, the U_3O_8 phase can exist from $UO_{2.67}$ down to $UO_{2.62}$; if Ames x-ray observations are correct, its stability may perhaps extend to $UO_{2.50}$. There is no doubt that the same phase can exist also above $UO_{2.67}$. The density curve (Fig. 5) shows no break at the composition $UO_{2.67}$, but continues to decrease linearly with increasing oxygen content up to $UO_{2.92}$. The rapid density drop between $UO_{2.92}$ and $UO_{3.00}$ may be due to the fact that the density value for UO_3 was obtained with amorphous trioxide.

According to Ames data (MP Ames 3), the x-ray diagrams confirm the gradual transition from U_3O_8 to UO_3. Zachariasen (MP Chicago 2) pointed out that the hexagonal uranium lattice found by him in one crystalline form of UO_3, can be obtained from the orthorhombic uranium lattice of U_3O_8 by a gradual change in the parameters of uranium atoms. This makes a continuous transition between the two oxides both possible and plausible.

For some unknown reason, however, the products of partial thermal decomposition of UO_3, obtained by Fried and Davidson (MP Chicago 3), did not show parameters intermediate between those of UO_3 and U_3O_8 (cf. p. 43).

Biltz and Müller (1927b) have also measured the oxygen pressures ob-

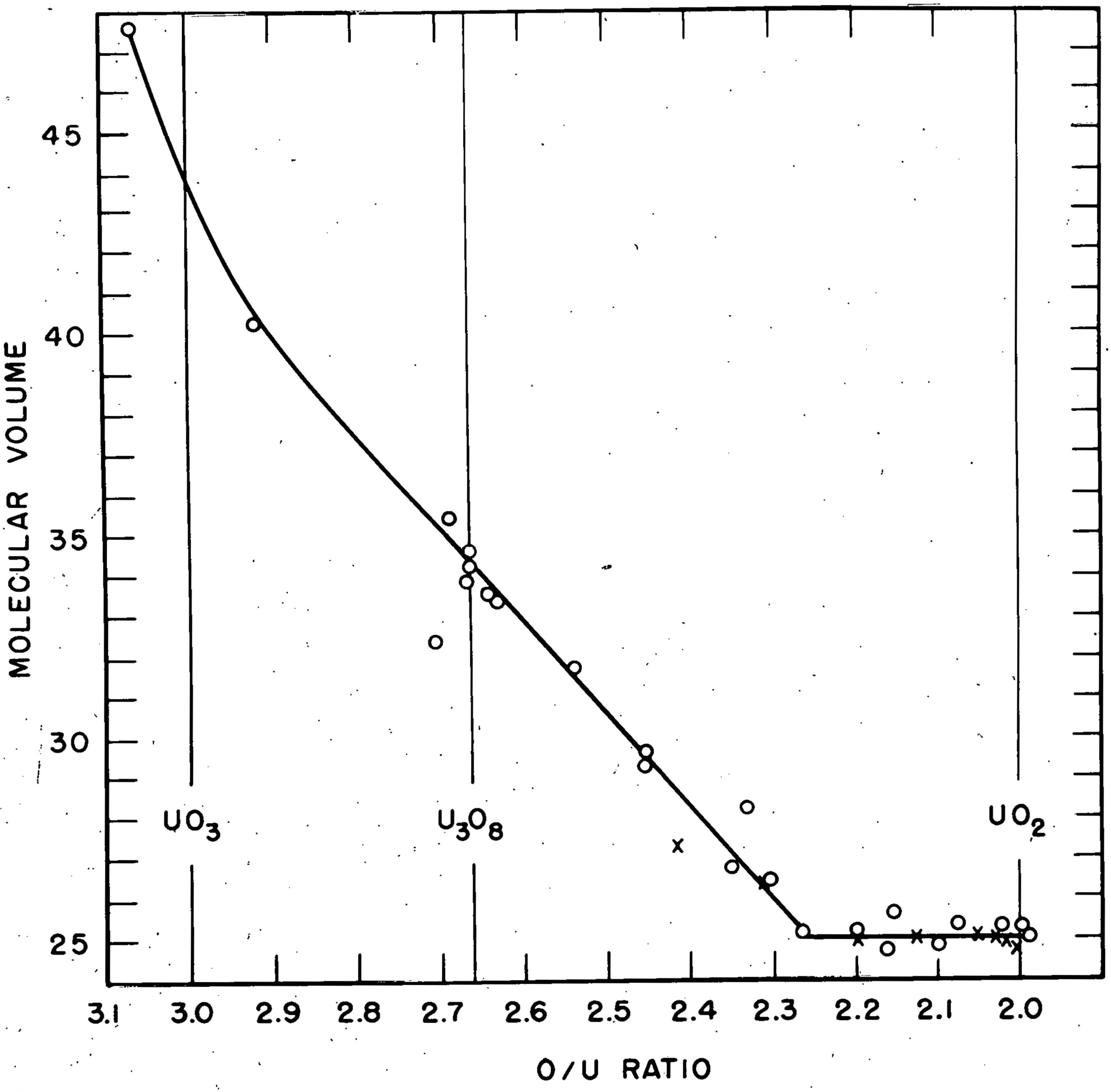

FIG. 5. CHANGE IN MOLECULAR VOLUME AS A FUNCTION OF URANIUM – OXYGEN RATIO. (FROM W. BILTZ AND H. MÜLLER, Z. ANORG. ALLGEM. CHEM., 163, 293 (1927)).

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tained by the decomposition of UO_3 to U_3O_8. The results are represented by six isothermals (438°C-650°C) in Fig. 6 and by the 10 mm isobar in Fig. 3.

In this region, as contrasted to that of oxide compositions below U_3O_8, the oxygen evolution is slow (perhaps in part because of comparatively low temperatures used) and complete equilibrium often cannot be reached even after several days of heating. Sometimes oxygen is evolved only if one starts with a pressure far below the equilibrium, while no gas liberation occurs at all if one begins with a pressure comparatively close to, but still below the equilibrium. In other cases induction periods of a day or more have been observed before gas evolution occurred. Delays of this type occurred particularly in the range $UO_{3.00}$ to $UO_{2.92}$ and may have been associated with the slow transition from amorphous trioxide to the crystalline lower oxides. "Induction" phenomena of this type may explain some contradictory observations concerning the thermal stability of UO_3 found in the literature. However, these discrepancies are probably mainly due to the different stability of the several crystalline forms of uranium trioxide (cf. p. 73).

Because of the slowness of de-oxygenation, most pressure values used in the construction of isothermals in Fig. 6 were obtained by extrapolation to infinite time, and it may be questioned how closely they approach the true equilibrium pressures. No check by approaching the equilibrium from the oxygenation side could be obtained since, e.g. $UO_{2.70}$ took up no oxygen at all in twenty-four hours under 72 mm pressure at 400°C. (The usual method of determination of uranium as U_3O_8 is based on the assumption that this oxide takes up no additional oxygen when ignited and cooled in air). However, the conversion of UO_3 to U_3O_8 is not thermodynamically irreversi-

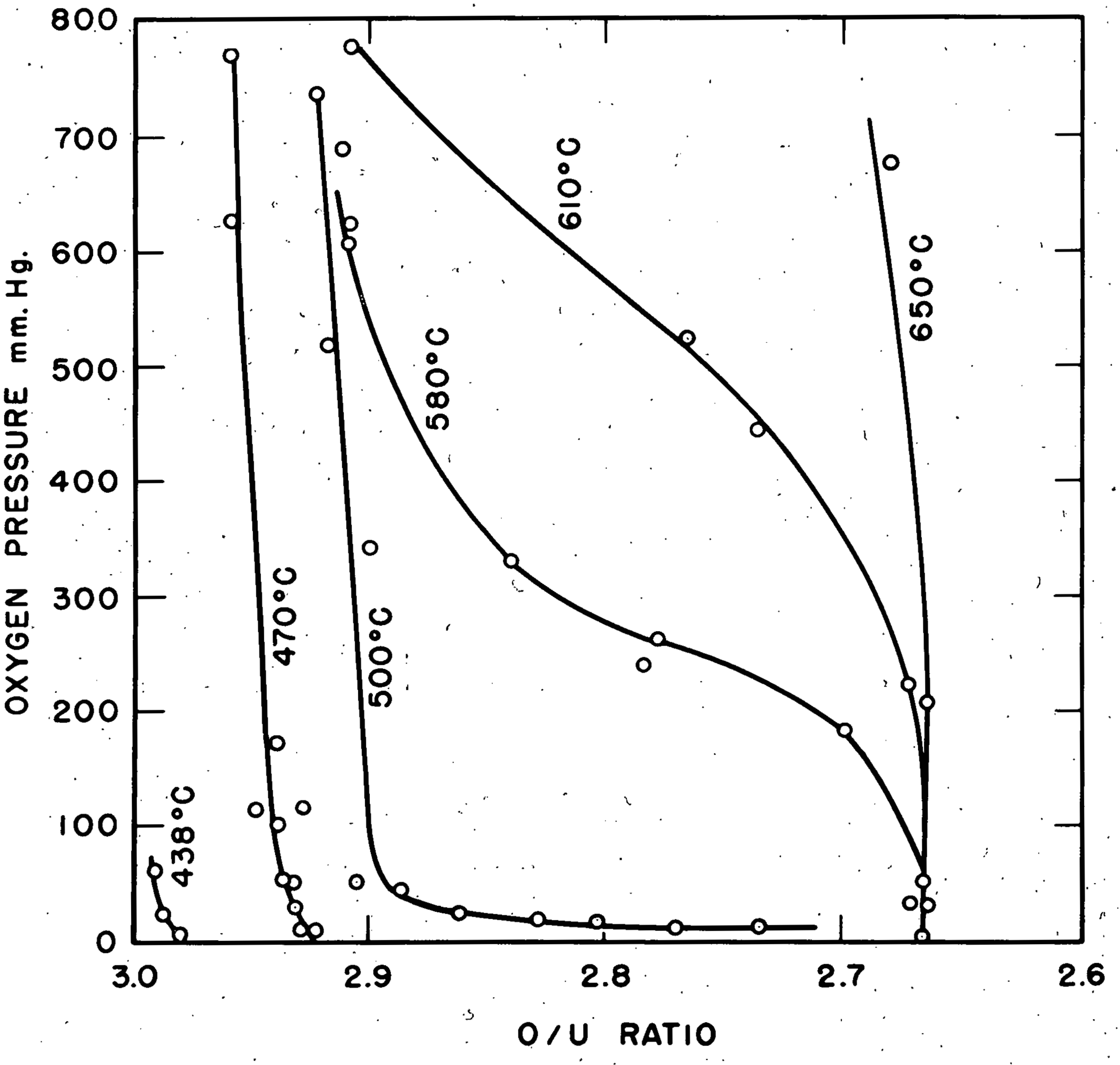

FIG. 6. DECOMPOSITION PRESSURES OF URANIUM-OXYGEN SYSTEM IN THE RANGE UO_3 TO $UO_{2.660}$.
(FROM W. BILTZ AND H. MÜLLER, Z. ANORG. ALLGEM. CHEM., 163, 266 (1927)).

ble. Finely dispersed U_3O_8, obtained by igniting uranyl oxalate, was found by Lebeau (1922) to take up oxygen at 350°C, changing its color within twelve hours from dark grey to orange-brown. This was confirmed by Biltz and Müller (1927a) who found that the product actually had a composition close to UO_3. Preparations of U_3O_8 ignited at 800°C were, on the other hand, "dead" burnt and took up no oxygen. Fried and Davidson (MP Chicago 3) found that ignited U_3O_8 can be converted to UO_3 by heating to 500°C under 28 atm oxygen for one or several days; the color changed in this case from black to deep red.

Biltz and Müller saw another illustration of the reversibility of the reaction:

$$3UO_3 \rightleftharpoons U_3O_8 + \tfrac{1}{2}O_2 \qquad (2)$$

in the existence in nature of yellow UO_3 minerals, such as gummite or rutherfordite which they thought should be interpreted as oxidation products of U_3O_8 minerals (cf. p. 101).

Even if the reversibility of the conversion of UO_3 to $U_3O_8 + O_2$ at the temperatures used is to be considered as certain, the question whether the oxygen pressures determined by Biltz and Müller actually were equilibrium decomposition pressures or not, remains open. Biltz and Müller were satisfied that they were at least not far off the equilibrium because the heats of decomposition derived from the pressure isothermals agreed well with those determined by direct calorimetric measurements (cf. below p. 72).

Fig. 6 shows no region of constant pressure between $UO_{2.67}$ and UO_3 at temperatures above 580°C. This clearly indicates a monophasic system. Below 580°C Brewer (MP Berkeley 1) interpreted Biltz's results as indicating the existence of a diphasic region extending from $UO_{2.67}$ to $UO_{2.92}$ and of a monophasic region with rapidly changing pressure between $UO_{2.92}$

and $UO_{3.00}$. He suggested that at the lower temperatures the trioxide used by Biltz and Müller was amorphous, and its composition could be changed continuously only down to $UO_{2.92}$ where a crystalline lower oxide phase began to form itself; at the higher temperatures (500°C and above) UO_3 might have become crystallized, and this made a continuous transition all the way from UO_3 to U_3O_8 possible.

1.5 The Range above UO_3. Table 1 indicates that some oxygen in excess of the composition $UO_{3.00}$ can be taken up by uranium trioxide, but this uptake leads to a rapid "swelling" of the crystal structure and the binding becomes very loose. The UO_x range above $x = 3.00$ is not very well known. Attempts to obtain water-free uranium peroxide, UO_4, have failed. However, Brown University observers (Brown 1) found that when $UO_4 \cdot 2H_2O$ was heated to 130°C for twenty-four hours and UO_4 was about one half decomposed to UO_3, an increase in temperature to 300°C led to loss of all water without further loss of oxygen, leaving an anhydrous compound with an average composition close to $UO_{3.5}$. This compound is a per-compound different in properties from the peroxide $UO_4 \cdot 2H_2O$; in contact with water or acid, it decomposes with evolution of oxygen and formation of hydrated UO_3. An anhydrous uranium per-compound also was obtained at Brown University (Brown 2) by calcination of $(NH_4)_2U_2O_7$ in a rapid stream of oxygen. At 250°C-350°C ammonia and water were evolved; the temperature was then raised to 550°C and a red powder, which appeared to be stable at high temperatures, was produced. It had the composition $UO_{3.14}$ to $UO_{3.38}$ and liberated oxygen in contact with water.

2. Physical Properties of Anhydrous Uranium Oxides

2.1 UO

2.2 UO_2

2.3 U_2O_5 (?)

2.4 U_3O_8

2.5 UO_3

2.6 UO_4

2. PHYSICAL PROPERTIES OF ANHYDROUS URANIUM OXIDES

2.1 UO. The properties of uranium monoxide are not well known. It has been described (MP Berkeley 1) as grey and brittle and having a metallic lustre. Table 2 contains the lattice constants found by different observers:

TABLE 2

LATTICE CONSTANTS OF UO

Composition	Lattice Constants of UO (Å)	Density g/cc	Reference
UO + U	4.91 ± 0.01	14.2 ± 0.1	(MP Ames 3)
	4.91	14.2	(British 1)
	4.93	14.0	(Battelle 1)
UO + UO_2	4.930 ± 0.001	14.0 ± 0.01	(MP Ames 10)

The lattice constant of UO is not known as exactly as the last figure in Table 2 seems to indicate because the sample used may possibly have contained some carbide or nitride.

Differentiation between rocksalt and zincblende structures is not easy when the two components are as different in mass as uranium and oxygen; however, the available evidence favors the rocksalt structure (MP Ames 3).

According to Brewer (MP Berkeley 1) UO is more volatile than UO_2; he estimated on the basis of general analogies that its vapor pressure may be of the order of 10^{-5} atm at 2000°K.

2.2 UO_2.

(a) Crystal Structure. Table 3 gives a summary of the crystal structure analyses of the fluorite-type UO_x phases with x from 1.75 to 2.3. According to p. 9 , $UO_{1.75}$ may be either a separate compound (U_4O_7) or the lower end of a continuous series of solid solutions extending upwards to $UO_{2.30}$. If U_4O_7 does exist as a stable compound (in respect to dismutation to UO_2 and UO), its heat of formation must be larger than the sum of the heats of formation of $3UO_2$ and UO, i.e. >925 ± 30 kcal per mole (132 ± 4 kcal per oxygen atom).

TABLE 3

CRYSTAL LATTICE OF UO_2

Preparation	Constant (A)	ρ (g/cc)	Observer
?	5.47	--	Goldschmidt (1923)
?	5.48	--	Van Arkel (1924)
"very pure sample"	5.4568 ± 0.0005	10.96 ± 0.01	(MP Chicago 4)
$UO + UO_2$	5.461 ± 0.001	--	(MP Ames 2,4)
$UO_{2.00}$ (Ames)	5.4586 ± 0.008	10.97	
$UO_{2.10}$	5.437 ± 0.001	11.18	
$UO_{2.20}$	5.433 ± 0.001	11.27	
$UO_{2.30}$ (with U_2O_5)	5.4297 ± 0.0008	11.36	
$UO_2 + 5\% U_3O_8$	5.464 ± 0.002	12.096	(SAM Columbia 1)
$UO_{2.00}$	5.460	--	(MP Chicago 1)
$UO_{1.75}$	5.477	--	

The crystal habitus of UO_2 has been described as follows:

Arfvedson (1824) - microscopic regular octahedra.

Péligot (1842) - metallic lustrous scales.

Hillebrand (1893a) - fine, strongly reflecting octahedra.

Aloy (1900) - rhombic tablets, usually rounded on four corners.

Hofmann (1915) - brilliant cubes.

The crystals of UO_2 are isomorphous with those of ThO_2; the two oxides form mixed crystals (Hillebrand, 1893a).

(b) Density. In addition to the systematic data by Hillebrand, Biltz and Müller given in Table 1, the following determinations of UO_2 density can be quoted:

TABLE 4

DENSITY OF UO_2

Observer	Reference	g/cc	Packing density g/cc	Remarks
Ebelman	(1842)	10.15	--	UO_2 from oxalate
Hillebrand	(1893)	10.95-11.0	--	cf. Table 1
Raynaud	(1912)	8.2	--	Amorphous product from oxalate + H_2
Biltz and Müller	(1927c)	10.8	--	Average for $UO_{2.00}$ to $UO_{2.26}$ (cf. Table 1)
UCRL	(UCRL 1)	--	3.76	Mallinckrodt powder, not tapped
"	(UCRL 1)	--	4.51	Mallinckrodt powder, tapped
Columbia U.	(SAM Columbia 2)	10.28	4.96	
Ames Group	(MP Ames 5)	10.9-11.1	--	
"	(MP Ames 5)	10	--	Melted, sintered at 2200°C
"	(MP Ames 6)	8.11	--	Sintered at 1400°C-2000°C
Columbia U.	(SAM Columbia 3)	10.37	--	Mallinckrodt product, 98.5 per cent UO_2; $44-53\mu$, degassed
"	(SAM Columbia 3)	9.30	--	Same, not degassed
"	(SAM Columbia 3)	10.47	--	$1-2\mu$, degassed

The difference in density between degassed and non-degassed powder is related to the capacity of UO_2 to take up gases (studied by Schmidt, 1928). Density can be increased, e.g. from 10.4 to 10.6, by prolonged heating to 130°C (Biltz and Müller, 1927c).

(c) Hardness. The scratch hardness of UO_2 is 3.5 on Mohs scale; it depends on previous history of the oxide (SAM Columbia 4).

(d) Melting Point. Ruff and Goecke (1911) found 2176°C (under nitrogen), while Friederich and Sittig (1925) gave 2500°C-2600°C for the melting point of UO_2.

(e) Vapor Pressure. Vapor pressure measurements of UO_2 were made at Chicago (MP Chicago 5) by the effusion method using α counting as the analytical method. The results are shown in Table 5.

TABLE 5

VAPOR PRESSURE OF UO_2

T°K	t°C	UO_2 evaporated* (10^{-8} g)	Evaporation time (min)	p calculated in 10^{-3} mm Hg
1873	1600	45	180	0.071
2023	1750	126	23	1.7
2073	1800	825	60	4.0
2173	1900	875	15	18
2273	2000	2300	10	72

* Hole 0.058 cm in diameter.

The data in Table 5 permits one to estimate that the heat of vaporization of UO_2 must be about 137 kcal/mole. Brewer gave, in his compilation of thermodynamic data (MP Berkeley 1), an estimated value for the vapor pressure of UO_2 ($p_{O_2} = 10^{-8}$ atm at 2000°K) which is much lower than the empirical values in Table 5.

Oxides with an average composition $UO_{>2.20}$ have a measurable rate of sublimation at temperatures much lower than those used in the experiments summarized in Table 5. According to Biltz and Müller (1927) brownish sublimates, which were obtained when $UO_{2.30}$, $UO_{2.46}$ and $UO_{2.67}$ were heated to 1300°C, had compositions between $UO_{2.15}$ and $UO_{2.17}$ while the residues had the compositions between $UO_{2.16}$ and $UO_{2.21}$.

Although the vapor pressure of the oxide probably increases with increasing oxygen content, the decomposition pressure of oxygen increases even more rapidly, and high oxygen pressure above the oxide interferes with its sublimation. This may explain the reason why (with pumping velocities available to Biltz and Müller) no sublimate was obtained when the composition of the solid was $UO_{>2.6}$. The mechanism of sublimation can perhaps be visualized as follows: in the decomposition of U_3O_8 molecules of a higher and relatively volatile oxide (e.g. UO_3) are formed. In a sufficiently high vacuum these molecules have a chance to evaporate. They decompose, in contact with cold surfaces, into oxygen and $UO_{2.15}$ (this being the phase in equilibrium with low pressure oxygen at moderately high temperatures).

(f) Specific Heat and Entropy. Regnault (1840) gave 0.619 x 10^{-3} cal/g (corresponding to 16.7 cal/g mole) as the average specific heat of UO_2 between 0°C and 100°C. The first detailed studies of the thermodynamic constants of uranium dioxide were carried out a hundred years later at the Pacific Branch of the U. S. Bureau of Mines at Berkeley (Nat. Bur. Standards 4,5).

The results are represented in Tables 6 and 7.

TABLE 6

SPECIFIC HEAT OF UO_2 AT LOW TEMPERATURES (Nat. Bur. Standards 4)

(Mallinckrodt material, containing 0.7 per cent UO_3)

T°K	Cp in cal/(mole °K)	T°K	Cp in cal/(mole °C)	T°K	Cp in cal/(mole °K)
15	0.378	31	2.280	170	11.10
16	0.473	32	2.261	180	11.57
17	0.574	35	2.425	190	12.04
18	0.687	40	2.637	200	12.47
19	0.815	50	3.365	210	12.86
20	0.968	60	4.103	220	13.23
21	1.148	70	4.841	230	13.56
22	1.358	80	5.563	240	13.87
23	1.599	90	6.298	250	14.17
24	1.900	100	6.958	260	14.44
25	2.270	110	7.619	270	14.69
26	2.715	120	8.276	280	14.94
27	3.478	130	8.923	290	15.16
28	6.230*	140	9.518	300	15.38
29	8.645*	150	10.07		
30	5.150*	160	10.60		

* These values uncertain because of the rapid change of heat capacity in this region.

The heat capacity curve of UO_2 has a peak between 15°K and 50°K (cf. Fig. 7) with a maximum value of 9 cal/(mole °K) at 28.6°K. The "extra" entropy corresponding to this peak was estimated as 0.87 e.u.; it can be attributed to a magnetic transformation (cf. p. 32).

TABLE 7

HEAT CONTENT OF UO_2 (Nat. Bur. Standards 5)

t°C	$H_T - H_{298.16}$ cal/(g mole)	C_p	t°C	$H_T - H_{298.16}$ cal/(g mole)	C_p
400	1650		1000	13280	
		18.00			20.40
500	3450		1100	15320	
		18.85			20.70
600	5335		1200	17390	
		19.35			21.00
700	7270		1300	19490	
		19.70			21.30
800	9240		1400	21620	
		20.00			21.30
900	11240		1500	23750	
		20.40			

The following equation was derived by Berkeley Bureau of Mines observers to represent the heat content of UO_2 in the range 300°K-1500°K:

$$(3) \qquad H_T = H_{298.16} + 19.77\,T + 0.546 \times 10^{-3}\,T^2 + \frac{4.68 \times 10^5}{T} - 7513$$

By differentiation one obtains for the heat capacity

$$(4) \qquad C_p = 19.77 + 1.092 \times 10^{-3}\,T - 4.68 \times 10^5\,T^{-2}$$

MacWood and Altmann (UCRL 2) gave equation (5) as an interpretation of the data of Moore, Kelley and Maier:

$$(5) \qquad C_p = 18.45 + 2.431 \times 10^{-3}\,T - 2.272 \times 10^5\,T^{-2}$$

The entropy at 298.1°K was estimated at Berkeley Bureau of Mines (Nat. Bur. Standards 4) by graphical integration (using, below 15°K, the

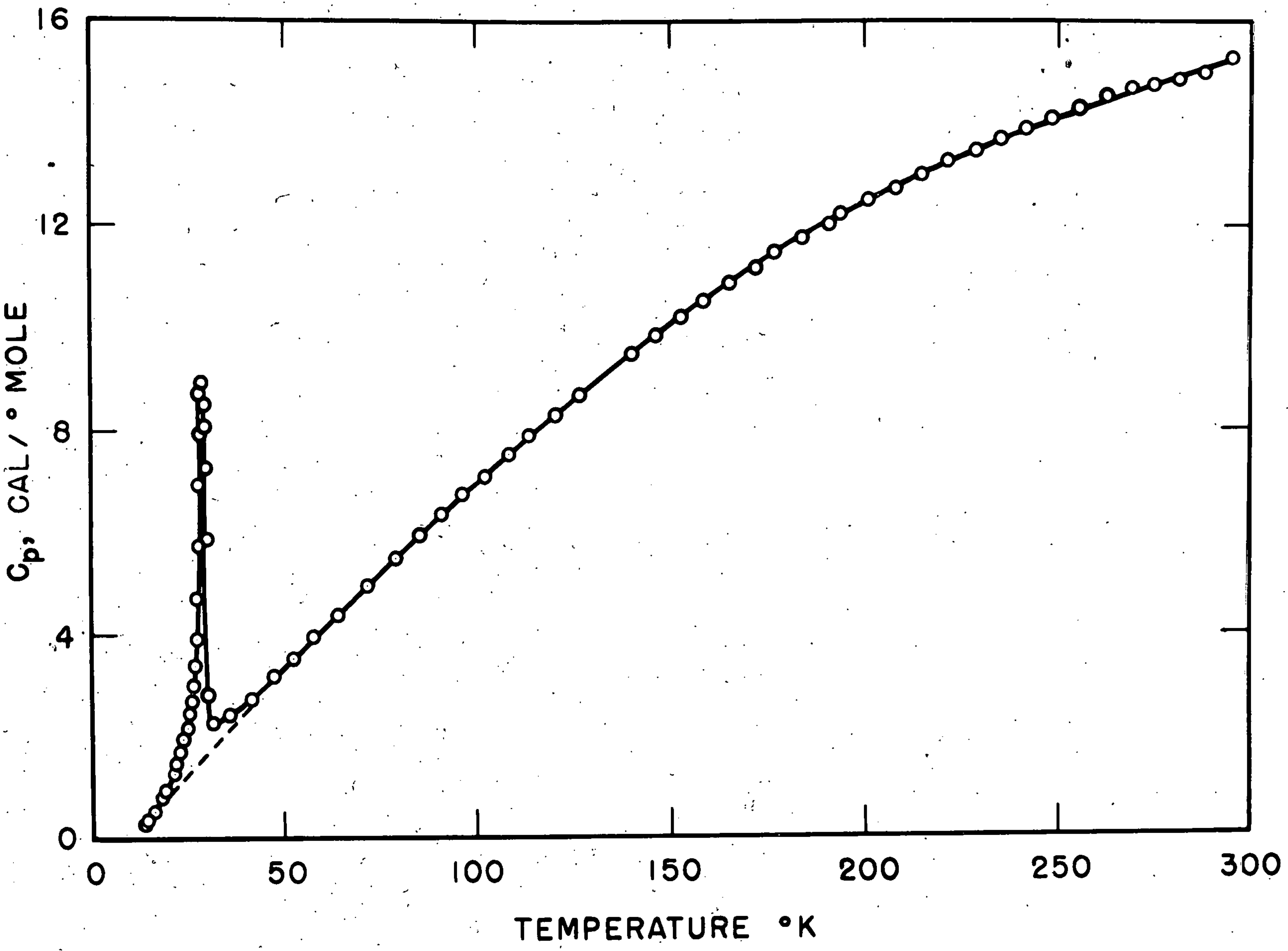

FIG. 7. HEAT CAPACITY OF UO_2.

Debye function with $\Theta = 160°K$) as follows:

$$S_{298.1°K} = 18.63 \ (\pm 0.1) \text{ E. U.}$$

Brewer (MP Berkeley 1) calculated the additional entropy values shown in Table 8.

TABLE 8

ENTROPY OF UO_2 (after Brewer)

T°K	500°	1000°	1500°
$(F_T-H_{298})/T$ cal/°K mole	20.5	28.1	34.3
S_T-S_{298} cal/°K mole	8.9	22.8	31.6

(g) Thermal Conductivity. The values shown in Table 9 were found at Princeton (Princeton 1,2,3) for UO_2 powder.

TABLE 9

THERMAL CONDUCTIVITY OF UO_2

Reference	(Princeton 1)	(Princeton 1)	(Princeton 2)	(Princeton 2)	(Princeton 2)	(Princeton 3)
t°C	50	100	20-225	270-610	18-160	
K in 10^{-4} cal/(sec. sq.cm.°C)	3.5	3.4	3.4	1.9	3.3*	50±5**

* Powder pressed to $\rho = 6$.

** Sintered.

(h) Electrical Properties. Similar to all dark colored oxides, UO_2 is a semi-conductor. Its conductivity depends strongly on exact composition, purity and degree of agglomeration (apparent density). The lowest conductivities were observed by Friederich and Sittig (1925). At room temperature they found, using a rod made of brown UO_2 sintered in hydrogen at 1100°C, a specific conductivity of only 4×10^{-8} $(\Omega\ \text{cm})^{-1}$ and a specific conductivity of about 3×10^{-5} $(\Omega\ \text{cm})^{-1}$ ~~was~~ found with a rod made of "dark blue" UO_2 (cf. pp. 33 and 34) sintered in nitrogen (also at 1100°C). These results indicate that conductivity decreases with progressive approach to the composition $UO_{2.00}$. It may be questioned whether it was the presence of "excess" oxygen or other conditions (i.e., a more compact form of the oxide, or better electrical contact) which were mainly responsible for the considerably higher conductivities observed by LeBlanc and Sachse (1930), Hartmann (1936), Meyer (1933) and by Ames observers (MP Ames 6). The results of these authors are collected in Table 10. At room temperature the values range from 2.4×10^{-4} to as much as 0.1 $(\Omega\ \text{cm})^{-1}$. Meyer obtained confirmation that uptake of oxygen in excess of the formula $UO_{2.00}$ (by heating a UO_2 sample previously ignited in high vacuum to $\sim 500°C$ in 1 - 100 mm O_2) increases its conductivity from 3×10^{-4} or 3×10^{-3} $(\Omega\ \text{cm})^{-1}$ before the treatment to about 1.2×10^{-2} $(\Omega\ \text{cm})^{-1}$ after it.

Meyer (1933) gave equation (6) for the electrical resistivity of UO_2:

$$R = 0.1804\ e^{1367/T} \qquad (6)$$

and found that the oxygen treatment leaves the factor before the exponential practically unchanged but decreases the "activation energy" by 20-30 per cent.

Hartmann (1936) pointed out that the increase of conductivity with the addition of "extra" oxygen puts UO_2 into the class of "hole conductors" in which the conductivity is due to the fact that some metal ions are missing from the lattice (their charge being taken over by other metal

TABLE 10

ELECTRICAL CONDUCTIVITY OF UO_2

t°C	Conductivity K in $10^{-3}/(\Omega\ cm)$ Hartmann (1936)	t°C	Conductivity K in $10^{-3}/(\Omega\ cm)$ Ames (MP Ames 6)
-60	2.09	28	$46.7^{(1)}$; $61^{(2)}$ $95^{(3)}$; $114^{(4)}$
-46	3.16	110	80.6
-25	5.25	157	118
-15	7.08	295	173
12	11.7	478	247
20	12.7	793	403
		992	1282
	LeBlanc and Sachse (1930)		Meyer (1933)
20	0.24	22	9.3
50	0.4	40	14.0
100	1.0	60	20.5
150	5.0	80	29.5
200	10	96	37.2
250	15	131	56.8
300	25	185	73.0
350	35	182	94
400	40	203	126
450	55	270	171
500	70	327	235

(1) Pressed and sintered at 1900°C-2000°C, $\rho_{app.} = 8.11$ g/cc
(2) ρ apparent 7.78 g/cc
(3) " 8.11 g/cc
(4) " 9.17 g/cc

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ions which temporarily assume a higher valency state, e.g., that of U^{6+}). He confirmed this hypothesis by measurements of the Hall effect in UO_2 (the sign of this effect permits one to distinguish "hole conductors" from "excess electrons" conductors).

The hypothesis that the oxides $UO_{>2.00}$ (up to $UO_{2.30}$) may be deficient in uranium, rather than containing extra oxygen, was discussed on p. 10 from the point of view of x-ray observations, and it was pointed out that density values do not permit the formulation of $UO_{2.30}$ as $U_{0.85}O_2$. However, it may be that a small deficit of uranium exists (independently of the presence of extra oxygen) and that this deficit may be the main cause of increased electric conductivity. Hartmann estimated from the Hall effect that his "oxygenated" UO_2 preparations contained about 3×10^{18} "disturbanse centers". This means that only about one in 10^5 uranium atoms was missing, a fraction which is not detectable by density measurements.

Wahlin (1932) investigated the ion emission of a UO_2 coated tungsten wire. The ions emitted included U^+ and probably also UO^+. The photoelectric effect of UO_2 was investigated by Pochettino (1932).

(i) Magnetic Properties. The magnetic data on UO_2 are listed in Table 11. Fig. 8 gives recent results by Haraldsen and Bakken (1940). The χ versus T curve can be represented by the Curie-Weiss equation $\chi = C/(T - \Theta)$, with $\Theta = -320$°K (according to Sucksmith) and $\Theta = -180$ (according to Haraldsen and Bakken).

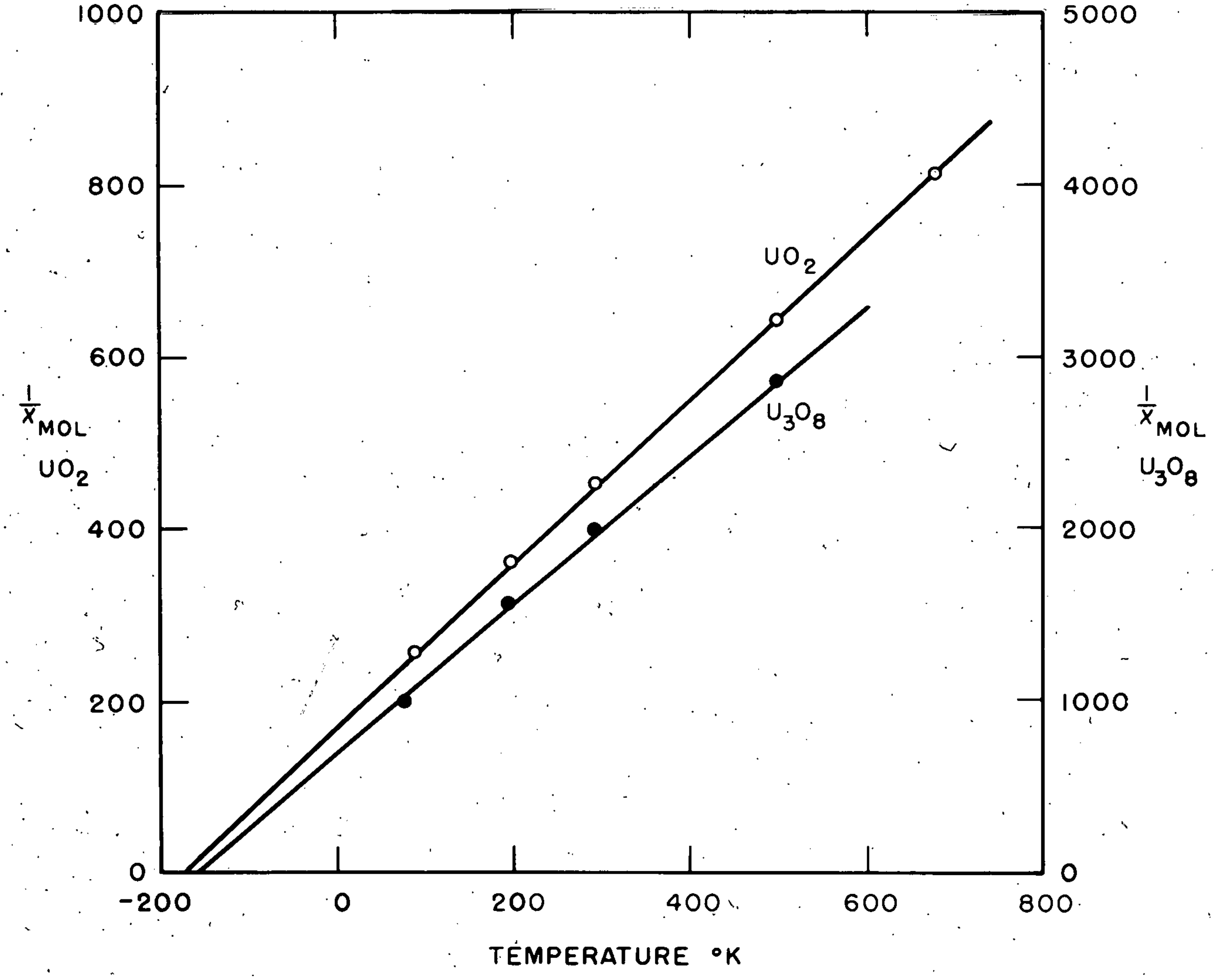

FIG. 8. MAGNETIC SUSCEPTIBILITY OF URANIUM DIOXIDE AND TRI-URANIUM OCTAOXIDE. (FROM H. HARALDSEN AND R. BAKKEN, NATURWISSENSHAFTEN, 28, 127 (1940)).

TABLE 11

MAGNETIC SUSCEPTIBILITY OF UO_2

Observer	t°C	Specific Susceptibility χ_{sp} (10^{-6} cgs)	Volume Susceptibility χ_{vol} (10^{-6} cgs)	Molar Susceptibility χ_{mol} (10^{-3} cgs) (corrected for diamagnetism)
Wedekind (1915)	17	7.51	--	--
Meyer (1899)	16	--	2.46	--
Sucksmith (1932)	-183	--	--	5.96
	- 75	--	--	4.70
	17	--	--	3.96
	97	--	--	3.51
	157	--	--	3.21
	226	--	--	2.75
	275	--	--	2.43

The value of the constant C found by Sucksmith corresponds to a magnetic moment of n_B = 4.4 Bohr magnetons (calculated by Haraldsen and Bakken) while the value given by Haraldsen and Bakken indicates a moment of n_B = 2.92 magnetons. The latter is very close to the theoretical value for pure spin magnetism of the U(IV) ion (n_B = 2.83). It will be noted that Sucksmith used in his calculation of n_B for U^{4+} only the values obtained with $U(SO_4)_2$ and with UCl_4 at low temperatures, which gave n_B = 3.2 and 2.8 respectively.

(3) Color. The color of uranium dioxide varies from brown to black. According to Lebeau (1922c), pure crystalline UO_2 is a brown powder, independent of the method of preparation. Biltz and Müller (1927d) obtained by reduction with hydrogen brown UO_2 from green U_3O_8, and dark

brown UO_2 with a slight violet tinge from black U_3O_8. Solid solutions of the type of $UO_{2.10}$-$UO_{2.30}$, obtained by the decomposition in vacuum of U_3O_8, are black. Oechsner de Coninck (1902, 1904) described a "brick-red" modification of UO_2 obtained by decomposition of UO_2Br_2 (cf. p. 112) but it is not quite certain that it was not a higher oxide (UO_3 ?). Friederich and Sittig (1925) obtained a "blue" dioxide by heating U_3O_8 to 1100°C in a stream of nitrogen. From what we know of the decomposition pressure of uranium oxides (p. 71) this preparation certainly was not $UO_{2.0}$, but rather $UO_{2.15}$; it might also have contained nitrogen.

2.3 $\underline{U_2O_5}$. It was mentioned on p. 13 that Ames x-ray data indicate the existence of an oxide U_2O_5, but that Biltz' tensimetric data, obtained at 1160°C, do not confirm it. If a homogeneous phase U_2O_5 actually does exist at room temperature, it could represent the lower limit of the solid solutions range extending upward to and beyond U_3O_8. The diffraction pattern of U_2O_5 (as observed in a product obtained by heating together equal amounts of U_3O_8 and UO_2) is, according to Ames observers (MP Ames 7), similar to but not identical with that of U_3O_8. It can be interpreted by means of an orthorhombic unit with the parameters a = 6.72A, b = 3.96A and c = 4.13A (± 0.01A). X-ray examination of a U_2O_5 single crystal (needles, obtained accidentally together with octahedral crystals of $UO_{2.30}$ by thermal decomposition of UO_2Cl_2 at 900°C) showed that the above dimensions refer to a pseudo-unit; in the complete unit the $\underline{b}$ parameter must be trebled and the $\underline{c}$ parameter doubled. The dimensions of the true U_2O_5 unit therefore are

$$a = 6.72 \pm 0.01A; \quad b = 11.88 \pm 0.03A \quad \text{and } c = 8.26 \pm 0.02A.$$

This unit contains twelve uranium atoms (as against two in the pseudo-unit) in two groups:

four U_I-atoms in positions (000), (½½0), (000) and (00½); and

eight U_{II}-atoms in positions (000), (½½0), (0 1/3 0) and (0 1/3 ½).

The positions of the thirty oxygen atoms in the unit cell probably are the same as in U_3O_8 (although two positions must be left empty since U_3O_8 contains thirty-two oxygen atoms for twelve atoms of uranium). The calculated x-ray density of U_2O_5 is 8.33 g/cc. It was mentioned above that no such low density appears in the density measurements collected in Table 1.

2.4 U_3O_8.

(a) Crystal Structure. The crystal lattice of the oxide U_3O_8 was described by Zachariasen (MP Chicago 6) as containing two uranium atoms and 5.33 oxygen atoms in an orthorhombic unit, with the dimensions a = 6.70 ± 0.01A, b = 3.98 ± 0.01A and c = 4.14 ± 0.01A. These values are very close to the above-given dimensions of the pseudo-unit of U_2O_5. According to Ames data (MP Ames 2,3), the b-parameter of U_3O_8 also must be trebled to obtain the correct unit dimensions. Consequently, the true unit cell of U_3O_8 contains six atoms uranium and sixteen atoms oxygen and has the dimensions a = 6.70 ± 0.01A, b = 11.94 ± 0.03A and c = 4.14 ± 0.01A. Table 12 shows the results of precision measurements made at Columbia University (SAM Columbia 1). All three measurements agree within ± 0.05 per cent. The six uranium atom positions in the U_3O_8 unit cell are (000), (½½0) (000), (0 1/3 0) (0 −1/3 0). The probable oxygen positions are:

four O_I-atoms in (000), (½½0), (0 1/3 ½); and

twelve O_{II}-atoms in (000), (½½0), (1/3 0 x), (1/3 1/3 x) (1/3 2/3 x),

with x = 0.17.

TABLE 12

CRYSTAL STRUCTURE OF U_3O_8

Preparation	a_o (A)	b_o (A)*	c_o (A)	ρ(g/cc)
$UO_4 \cdot 2H_2O$, heated 40 hrs. at 700°C	6.7023 ± 0.0005	3.9803 ± 0.0004	4.1385 ± 0.0007	8.39
$UF_6 + H_2O \rightarrow$ ppt, dried 40 hrs. at 700°C	6.7030 ± 0.0006	3.9812 ± 0.0004	4.1407 ± 0.0006	8.39
$UF_6 + HIO_3 \cdot aq \rightarrow$ ppt dried 40 hrs. at 700°C	6.7036 ± 0.0007	3.9815 ± 0.0004	4.1406 ± 0.0005	8.39

* 1/3 of true value

(b) <u>Density</u>. The calculated x-ray density of U_3O_8 is 8.39 g/cc. The measured values are somewhat smaller (cf. Table 13).

TABLE 13

DENSITY OF U_3O_8

Observer	ρ g/cc	Preparation
Wedekind and Horst (1915)	7.193	--
Ebelmen (1842)	7.31	--
Biltz and Müller (1927c, cf. Table 1)	8.30	From $UO_4 \cdot 2H_2O$
Columbia University (SAM Columbia 3)	7.50	Mallinckrodt batch D, particle size 44-74μ, degassed
"	6.97	Same, not degassed
"	8.13	Same, particle size 1/2 μ, degassed

(c) Hardness. According to Columbia University observers (SAM Columbia 4) U_3O_8 has a hardness of 3.5 on Moh's scale, depending somewhat on history of the sample.

(d) Thermodynamic Properties. The following values of the specific heat have been determined (Table 14). In a summary report

TABLE 14

SPECIFIC HEAT OF U_3O_8

Observer	T °K	C_p cal/°C	
		per g	per mole
Donath (1879)	273 - 373	0.0798	67.2
Russell (1912)	82 - 195	0.0429	36.2
"	196 - 250	0.0616	52.0
"	276 - 314	0.0710	59.8
(Nat. Bur. Standards 6)	25 - 100	0.0750	63.3

from UCRL (UCRL 2) it is stated that "the heat capacity of U_3O_8 is known from 213°K to 333°K," but no data or reference is given. This paper gives equation (6), said to be derived from experimental data for U_3O_8 at low temperatures and from interpolated data at the higher temperatures (the interpolation being from the values for UO_2 and UO_3):

$$(6) \qquad C_p = 62.6 + 6.6 \times 10^{-3}\ T - 2.5 \times 10^{5}\ T^{-2} \text{ cal/mole}$$

The entropy of U_3O_8 was first estimated by Kelley (U. S. Bur. Mines 1) as 72.7 E.U. (at 298°K). Davidson (MP Chicago 7) gave S_{298} = 66 E.U., and also estimated values for $S_T - S_{298}$ and $H_T - H_{298}$ for 500°K, 800°K, 1100°K and 1300°K. Brewer (MP Berkeley 1) interpolated values for 1000°K and 1500°K, and also gave estimates for the function $(F_T - H_{298})/T$. These estimates are summarized in Table 15.

TABLE 15

ESTIMATED VALUES OF THERMODYNAMIC FUNCTIONS FOR U_3O_8

T °K	298	500	1000	1500
$H_T - H_{298}$ (kcal/mole)	0	12	42	81
$S_T - S_{298}$ (cal/mole °C)	0	28	72	105
$(F - H_{298})/T$ (cal/mole °C)	66*	70	96	117

* = S_{298}

(e) Thermoelectric Power. Bidwell (1914) measured the EMF of U_3O_8 against platinum with the cold junction at 165°C - 1155°C and the hot junction at 320°C - 1265°C. The EMF was positive (i.e., the current flowed from platinum to oxide through hot junction) up to about 700°C (temperature of hot junction) and changed its sign above this temperature.

(f) Electrical Properties

(1) Dielectric Constant. Keller and Lehmann (1934) found C = 41.77 for U_3O_8 powder pre-heated one hour to 200°C and pressed between two plates (10,000 atm).

(2) Electrical Conductivity. Like UO_2, the oxide U_3O_8 is a semi-conductor. However, according to LeBlanc and Sachse (1930), it differs from UO_2 by the occurrence of polarization which indicates that the conductance is not purely electronic in nature. This complication, added to the fact that the U_3O_8 preparations used by different observers

probably have varied considerably in their oxygen content, gives some explanation of the fact that the conductivities found by different observers differed by as much as a factor of 10^6. As in the case of UO_2, the lowest conductivities were observed by Friederich and Sittig (1925), who found that a U_3O_8 rod, sintered in oxygen at 1000°C, had a specific resistance as high as 40×10^6 Ω cm at room temperature; at 300°C the resistance was ten times smaller. LeBlanc and Sachse (1930) found much better conductivity in a sample obtained by oxidation of UO_2 in air at 500°C. Fischer and Rideal (1914) observed a still lower specific resistance (only about 2700 Ω cm at room temperature) in hydrated U_3O_8, obtained by electrolytic deposition and pressing; even higher conductivity was observed by Wiegand (1924) in a rod sintered at 1200°C. The results of LeBlanc and Sachse and of Wiegand are shown in Table 16.

TABLE 16

ELECTRIC CONDUCTIVITY OF U_3O_8

t°C	K in $10^{-4}\ \Omega\ cm^{-1}$		t°C	K in $\Omega\ cm^{-1}$	
	LeBlanc and Sachse (1930)	Wiegand (1924)		LeBlanc and Sachse (1930)	Wiegand (1924)
20	0.001	--	400	0.0007	--
50	0.0025	500	450	0.0014	--
100	0.0090	750	500	0.0024	1.88
150	0.030	--	600	--	2.95
200	0.15	2500	700	--	4.08
250	0.50	--	800	--	5.60
300	[illegible]	5000	900	--	7.86
350	3.	10500	950	--	9.35

(g) Magnetic Properties. U_3O_8 is paramagnetic. Early measurements of its magnetic susceptibility gave the values listed in Table 17 (uncorrected for diamagnetism):

TABLE 17

PARAMAGNETISM OF U_3O_8

Observer	Specific Susceptibility (15°C)	Volume Susceptibility (16°C)
Wedekind and Horst (1915)	0.95×10^{-6}	--
Meyer (1899)	--	$+ 0.351 \times 10^{-6}$

The recent results of Haraldsen and Bakken (1940) are shown in Fig. 8.

This figure shows that the paramagnetic susceptibility (corrected for diamagnetism) follows the Curie-Weiss law, $\chi = \frac{C}{T - \Theta}$

with a characteristic temperature $\Theta = -170°K$. The molar magnetic moment, calculated from the constant C, is $n_B = 1.39$ Bohr magnetons. This is very close to the theoretical value, $n_B = 1.42$ for $UO_3 \cdot U_2O_5$ (assuming spin magnetism of the ground state ^2F of the ion U^{5+} to be the only source of paramagnetism). In other words, U_3O_8 behaves in the magnetic field as if it contained hexavalent and pentavalent rather than tetravalent uranium. (For a discussion of this conclusion, see p.).

(b) Optical Properties. Color: U_3O_8 can be from olive-green to black-green or black. However, even black preparations give a green streak on porcelain. The color depends not so much on the exact composition as on the conditions of preparation (Zimmermann, Alibegoff and Krüss, 1886); the higher the temperature of ignition, the darker the sample. For example, U_3O_8 prepared by Biltz and Müller (1927) from $UO_4 \cdot 2H_2O$ below 800°C was moss-green while the oxide prepared at 900°C - 1000°C was almost black. The emission spectrum of U_3O_8(?) in the oxyhydrogen flame was observed by Huggins (1870) who found it to be the normal continuous spectrum of hot solids (cf. below). The infrared emission spectrum was observed by Coblentz (1908) who noted weak maxima at 2.8 and 3.4 μ.

The emissivity of "U_3O_8" was first investigated by Burgess and Waltenburg (1914, 1915). (Because of the instability of U_3O_8 at the temperatures used, the results of these experiments relate to oxides of unknown composition but certainly $UO_{<2.67}$). They found that the emissivity coefficient at 65 mμ, was 0.30 for the solid oxide at 1650°C and 0.31 for the liquid(?) at 1700°C. Wiegand (1924) found a total emissivity of 77-79 per cent of that of a black body. This ratio remained practically unchanged between 900°C and 1400°C. Nichols and Howe (1922) used U_3O_8 as standard in the study of the selective emissivity of other oxides in the assumption that the spectral distribution of the uranium oxide emission parallels closely that of a black body. However, the results of Philipps (1928) indicate that the emissivity of U_3O_8, similar to that of ceria and other oxides, is, in the blue (467 mμ), higher than that of a black body of the same "red brightness."

2.5 UO_3.

(a) Crystallization. Until recently UO_3 (usually obtained by ignition of $UO_4 \cdot 2H_2O$) was found to be amorphous (Goldschmidt and Thomasson, 1923a). Microcrystalline UO_3 preparations were first obtained at the Mallinckrodt Chemical Company by ignition of uranyl nitrate. British observers (British 2) found that UO_3 crystallizes on standing; two crystalline forms were identified. Fried and Davidson (MP Chicago 3,8) found that UO_3 can exist in at least three crystalline forms, orange hexagonal UO_3(I), red UO_3(II) and yellow UO_3(III). The last form ("Mallinckrodt oxide") is probably the most stable one.

Because UO_3 loses oxygen in air above 450°C (p. 78), the crystallization experiments of Fried and Davidson were conducted under high oxygen pressures (30-150 atm). The amorphous trioxide (or U_3O_8) was heated to 500°C - 750°C in closed pyrex or quartz tubes.

Table 18 shows the nature of the products obtained under different conditions. Phase I was analyzed by Zachariasen (see below). Phase III is that found in Mallinckrodt's oxide; it is the most stable of the three. The reason phase I is the first to be formed may be its crystallographic similarity to U_3O_8, which permits its formation from U_3O_8 by gradual uptake of oxygen.

TABLE 18

CRYSTALLIZATION OF UO_3

Substance treated	t °C	P_{O_2} (atm.)	Time hrs.	Phase obtained	x from oxygen uptake	x from weight change by ignition to U_3O_8
UO_3	450-500	28	12	I	—	—
U_3O_8	500-560	〃	36	I + II	2.97	3.048
U_3O_8	530-560	30	112	II + III	2.997	2.99
UO_3	530-560	30	112	I + II	—	—
U_3O_8	700-750	70-150	1.5-2	III	2.993	3.01

(b) Crystal Structure. Crystalline UO_3(I) obtained by heating amorphous, anhydrous UO_3 to 500°C for eight hours under 20 atm. oxygen pressure has, according to Zachariasen (MP Chicago 2), an hexagonal lattice with the parameters a = 3.963 ± 0.004A and c = 4.160 ± 0.008A. The space group is $C\bar{3}m$, and the oxygen atom positions around U(000) are as follows:

One O_I-atom in (00½); two O_{II}-atoms in (1/3 2/3 x), with x = 0.17. Each uranium atom has two nearest O_I-atoms at 2.08A distance and six O_{II}-atoms at 2.39A distance. The O_I atoms can be considered as "uranyl oxygens" although no UO_2 groups are present in the strucutre. Instead, there are endless "uranyl chains," - O - U - O - U - O - U . . . , stretching along the c-axis.

Fried and Davidson (MP Chicago 8) reported two x-ray measurements of partly de-oxygenated UO_3 which gave somewhat unexpected results. (Cf. Table 19). Contrary to expectation (cf. p. 16) the lattice constants at x = 2.82 and 2.96 were not intermediate between those at

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x = 2.67 and 3.00.

TABLE 17

LATTICE PARAMETERS OF UO_x (x = 2.67 to 3.00)

(all referred to ortho-hexagonal axes)

x	a_1 (A)	a_2 (A)	a_3 (A)
2.67*	6.70 ± 0.01	3.98 ± 0.01	4.14 ± 0.01
2.82	6.90 ± 0.02	3.91 ± 0.02	4.15 ± 0.02
2.96	6.90 ± 0.02	3.91 ± 0.02	4.15 ± 0.02
3.00*	6.864 ± 0.004	3.963 ± 0.004	4.160 ± 0.008

* after Zachariasen, cf. p. 35 and 43 .

The x-ray diffraction patterns of the forms UO_3(II) and UO_3(III) have not yet been analyzed but are different from those of hexagonal UO_3(I). According to Fried and Davidson (MP Chicago 3,8) three samples of UO_3, prepared at 350°C-400°C by vapor phase oxidation of U_3O_8 by nitric acid (CEW-TEC 1), gave two different x-ray patterns, both distinct from those of the above mentioned forms I, II and III. It is thus possible that UO_3 exists in as many as five crystalline allotropic forms.

(c) Density. The calculated density of UO_3(I) is 8.34 g/cc. Experimental density values are much lower; most of them refer to amorphous oxide, some perhaps to hydrates (e.g. $UO_3 \cdot H_2O$). (Cf. Section 3.3). For example, Wedekind and Horst (1915) found $\rho = 5.92$ (16°C), Beck (1928), $\rho = 7.29$ (15°C) and v. Schroeder (1922), $\rho = 7.37$ (25°C). Biltz and Müller (1927c) gave $\rho = 6.04$ (for $UO_{3.07}$) and $\rho = 7.07$ (for $UO_{2.92}$); while at Columbia (SAM Columbia 2) a value of $\rho = 7.54$ g/cc (25°C) was observed. Jenkins (UCRL 1) gave 3.63 as the packing density of untapped, and 4.26 as that of slightly tapped UO_3 powder.

(d) Vapor Pressure. As described on p. 14 , a certain volatility of uranium oxide in the two-phase region between $UO_{2.62}$ and $UO_{2.25}$, observed by Biltz and Müller above 1160°C, can be attributed to the disproportionation:

$$(7) \qquad U_3O_8 \longrightarrow UO_2 + 2UO_3,$$

and evaporation of UO_3. Above $UO_{2.62}$ the partial pressure of oxygen is so much higher than the vapor pressure of UO_3 that the evaporation of the oxide becomes too slow for observation. Brewer (MP Berkeley 1) estimated from the data of Biltz and Müller that at 1600°K, $p(UO_3)$ is 10^{-5} atm over $UO_{2.25}$ - $UO_{2.62}$, and 10^{-4} atm over pure UO_3.

(e) Thermodynamic Properties of UO_3. At the U. S. Bureau of Mines at Berkeley (Nat. Bur. Standards 1) the heat capacity of UO_3, probably in the form UO_3(III) (MP Chicago 3), was measured between 15°K and 300°K (Table 20). The entropy at 298.1°K was evaluated by graphical integration, using below 15°K the Debye function, with $\Theta = 140°K$;

$\int C_p \, d\ln T$	(15-300°K)	23.378
$\int$ Debye function	(0 - 15°K)	0.196
		23.57 ± 0.06 E.U.

In the same laboratory (Nat. Bur. Standards 5) the heat content at 300°K-900°K was measured, using a sample dehydrated at 600°C for seventy-nine hours (dissociation might have caused an error of ~1 per cent). The values lie on a smooth curve.

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TABLE 20

SPECIFIC HEAT OF UO_3

T°K	C_p cal/(mole degree)	T°K	C_p cal/(mole degree)
15	0.608	160	14.33
20	1.040	170	14.93
25	1.553	180	15.49
30	2.103	190	16.01
40	3.231	200	16.49
50	4.370	210	16.94
60	5.505	220	17.38
70	6.602	230	17.82
80	7.675	240	18.24
90	8.704	250	18.66
100	9.693	260	19.05
110	10.63	270	19.42
120	11.49	280	19.73
130	12.29	290	20.02
140	13.00	300	20.30
150	13.70		

TABLE 21

HEAT CONTENT OF UO_3

T°K	$H_T - H_{298.16}$ cal/mole	T°K	$H_T - H_{298.16}$ cal/mole
400	2080	700	8820
500	4280	800	11160
600	6510	900	13540

(8) $$H_T - H_{298.16} = 22.54\ T + 1.011 \times 10^{-3}\ T^2 + 3.29 \times 10^5\ T^{-1} - 7914 \quad (\pm\ 0.3\%) \quad \text{cal/mole}$$

By differentiation one obtains for C_p

(9) $$C_p = 22.54 + 2.022 \times 10^{-3}\ T - 3.29 \times 10^5\ T^{-2}.$$

Brewer (MP Berkeley 1) derived from these measurements the following values of the function $f = (F - H_{298})/T$:

TABLE 22

THE FUNCTION $f = \frac{F - H_{298}}{T}$ FOR UO_3

T°K	298	500	1000
f cal/degree	23.57*	25.7	34.4

* = S^o_{298}

(f) Thermal Conductivity. U_3O_8 powder, compressed by screws kept tight during the heating, was found by Princeton observers (Princeton 1,2) to have the following thermal conductivity:

TABLE 23

THERMAL CONDUCTIVITY OF U_3O_8

t°C	25 - 150	160 - 340	310 - 600
K in cal/(cm sec °C)	0.00067	0.00063	0.00061

(g) Electrical Properties. LeBlanc and Sachse (1930) found no measurable electric conductivity of UO_3 up to 300°C. The conductivity sometimes observed at room temperature, and which disappears at 100-150°C, can be attributed to uptake of moisture. The conductivity increases strongly at 350°C-490°C, particularly on prolonged heating; this may be due to the loss of oxygen and conversion into the lower, semi-conducting oxides. After thirty hours at 400°C, a product with an initial composition $UO_{2.9-3.0}$, showed a constant conductivity of 1.4×10^{-5}. Similar values were obtained by Guillery (1932).

The dielectric constant of UO_3 was measured at the Tennessee Eastman

Company (CEW-TEC 2) using an oxide cake washed free of electrolytes. Values obtained ranged from 1.86 (UO_3 dried to orange color at 150°C, $\rho = 2.0$ g/cc, 79.19 per cent uranium) to 4.36 (UO_3 "Mallinckrodt" brick red), and to as high as 9.41 - 11.4 (two brown UO_3 samples, Chem-723, B.T.).

(h) Magnetic Properties. Sucksmith (1932) found UO_3 to be diamagnetic. Other observers found, however, a small temperature-independent paramagnetism. Wedekind and Horst (1915) gave $+1.08 \times 10^{-4}$ as the specific susceptibility at 16°C and Meyer (1899), $+0.146 \times 10^{-6}$ as the volume susceptibility at the same temperature. Tilk and Klemm (1939) reported $\chi\,(\text{specific}) = +0.26 \times 10^{-6}$, $\chi_{molar} = + 74 \times 10^{-6}$; corrected for diamagnetism $\chi_{molar} = + 128 \times 10^{-6}$ (average of values obtained with UO_3 samples from nitrate, carbonate and peroxide). The diamagnetism values used for correction were 20×10^{-6} for U^{6+} and 11.25×10^{-6} for O^{2-}. Haraldsen and Bakken (1940) found $\chi_{molar} = + 157 \times 10^{-6}$ (corrected for diamagnetism).

(i) Color. Amorphous UO_3 powder prepared by ignition of $UO_4 \cdot 2H_2O$ has been described as "sulfur-yellow" (Biltz and Müller) and "bright orange" (Fried and Davidson). Hexagonal, crystalline UO_3(I), prepared by Fried and Davidson from the amorphous product, was somewhat lighter in color. The phase UO_3(II) obtained from amorphous UO_3 or U_3O_8 by heating to 500°C under 28 atm oxygen was deep red; the brick-red product that Oechsner and Coninck had obtained (cf. p. 98) by prolonged heating of orange UO_3 to 600°C in air may have been the same form. The phase UO_3(III), obtained by Fried and Davidson by more prolonged heating under still higher oxygen pressure and also present in Mallinckrodt's microcrystalline product obtained by ignition of uranyl nitrate, is bright yellow. The two new crystalline UO_3 forms, obtained by oxidation of U_3O_8 by N_2O_4 (p. 103), were brick-red (or orange) and yellow respectively.

The partly deoxygenated products of UO_3 were described by Fried and Davidson as tan ($UO_{2.96}$), tan-green ($UO_{2.82}$), and green-black ($UO_{2.70}$), thus showing gradual transition to the black U_3O_8 phase.

2.6 $\underline{\underline{UO_4}}$. This oxide is unknown in the anhydrous state; for physical properties of its hydrates, see this chapter, section 3.4(b), p. 65 . The product $UO_{3.5}$, obtained by Kraus and co-workers (cf. p. 19) and interpreted as $UO_3 + UO_4$, was described as a red powder.

3. Uranium, Oxygen, Water

3.1 UO_2 Hydrates.

3.2 U_3O_8 Hydrates.

3.3 UO_3 Hydrates.

- (a) Phase Relationships in the System UO_3/H_2O.
- (b) Thermodynamic Properties of UO_3 Hydrates.
- (c) Physical Properties of UO_3 Hydrates.
- (d) Hydration and Dehydration of UO_3.
- (e) Formation of UO_3 Hydrates by Hydrolysis and Electrolysis of Uranyl Salts.
- (f) Preparation of $UO_3 \cdot H_2O$ and $UO_3 \cdot 2H_2O$ from UO_2 and U_3O_8.

3.4 UO_4 Hydrates.

- (a) Dehydration of $UO_4 \cdot$aq.
- (b) Physical Properties of UO_4 Hydrates.

3.5 Uranium Oxide Hydrosols and Suspensions.

- (a) Uranium Oxide Hydrosols.
- (b) Uranium Oxide Suspensions.

3. Uranium Oxide Hydrates.

3.1 **UO_2 Hydrates.** Péligot (1842) observed the formation of a flaky, voluminous, reddish-brown precipitate by the reaction of ammonia with green U(IV) salt solutions. According to Zimmerman (1882) the precipitates formed by the action of alkalis or ammonia on U(IV) solutions are light-green at first, but are rapidly converted in the presence of air into brown U_3O_8 hydrates. Aloy (1901) found that the best method to obtain alkali-free, unoxidized uranium dioxide hydrate is to hydrolyze a dilute, air-free U(IV) chloride (or U(IV) acetate) solution by heating until it becomes colorless. The black precipitate formed is a basic salt but it can be washed free of anions with boiling water. After drying over H_2SO_4, the hydrate has the composition $UO_2 \cdot 2H_2O$. The U(IV) salt solutions can also be decomposed by illumination (Aloy and Rodier (1922). Rowell and Russell (1925) obtained a slimy black or greenish-black UO_2 hydrate by photochemical decomposition of a uranyl nitrate solution in ether. Black, crystalline $UO_2 \cdot 2H_2O$ was obtained by Aloy (1899) by the action of alkali on crystalline uranium (IV) sulfate.

According to Aloy (1899) moist, amorphous $UO_2 \cdot 2H_2O$ is oxidized in air, slowly in the cold, rapidly on heating, to $UO_3 \cdot H_2O$. Crystalline UO_2 hydrate, on the other hand, is stable in air for several days at room temperature; it is converted to green U_3O_8 by heating.

Columbia observers (SAM Columbia 5) found that $UO_2 \cdot xH_2O$ is dehydrated under water above 285°C to brown anhydrous dioxide. In air (SAM Columbia 6) the hydrate lost all water within one half hour at 200°C, suffering at the same time partial oxidation to U_3O_8.

Freshly prepared U(IV) hydroxide is readily soluble in acids, but loses solubility upon standing (Péligot, 1842 ; Rammelsberg, 1843 ; Hermann, 1861 ; Raynaud, 1911). The solutions contain colloidal aggregates or polymeric ions rather than simple U(IV) salts.

3.2 U_3O_8 Hydrate. The existence of a U_3O_8 hydrate first mentioned by Arfvedson (1822) was definitely established by Ebelmen (1842a). He prepared it by photochemical decomposition of uranyl oxalate. It is a flaky, brownish-violet precipitate, easily oxidizable in air. To avoid decomposition it must be dried in vacuum. Aloy (1900) recommended the use of uranyl acetate as starting material instead of the only slightly soluble oxalate. When an aqueous uranyl acetate solution containing ether or alcohol is exposed to light, a violet precipitate is formed which proves less easily oxidizable than the U_3O_8 hydrate obtained by Ebelmen from oxalate. Aloy and Rodier (1920) found that a similar violet precipitate is formed by all uranyl salt solutions (with a concentration of 1-5 per cent) when exposed to light in the presence of organic substances which can act as reductants (acetaldehyde, ether, alcohol, glucose). Immediately after precipitation, the hydroxide contains anions of the acid, but they can be washed out with boiling water. If uranyl salts of organic acids are used, no addition of extra organic reductants is necessary.

According to Columbia University observers (SAM Columbia 4) U_3O_8 does not react with water even after eleven days at 185°C. However, U_3O_8 prepared by ignition below red heat may contain UO_3, and therefore absorbs some water from the air to form $UO_3 \cdot 2H_2O$ (Lebeau, 1922) (Staehling, 1921).

The composition of the violet hydrate, obtained as described above, was given in the literature only as $U_3O_8 \cdot xH_2O$. According to Smith

(1879,1880) and Oechsner de Coninck and Camo (1901a) electrolysis of uranyl salt solutions leads first to yellow $U_3O_8 \cdot H_2O$ and then to black $U_3O_8 \cdot 2H_2O$. However, Pierlé (1919) asserted that the black deposit has the composition $UO_{3.3} \cdot 2H_2O$ rather than $UO_{2.67} \cdot 2H_2O$. (Cf. p. 118.) He considered the high potential of the electrode coated with this black hydroxide (cf. p. 79) as an additional argument against its interpretation as a U_3O_8 hydrate. The formation of a U_3O_8 hydrate deposit on uranium metal by electrolysis of uranyl nitrate solution was again investigated by Francis and Tcheng-Da-Tchang (1935) and Francis (1935).

Aloy (1900) found that amorphous, violet $U_3O_8 \cdot xH_2O$ does not become crystalline by freezing or heating under pressure. Drying in vacuum converts it into a solid black mass which can be ground to a black powder. Heated in nitrogen, this mass loses water without changing its appearance; but grinding after drying produces a green rather than black powder.

According to Aloy $U_3O_8 \cdot xH_2O$ is easily oxidized in air to UO_3 hydrate. It dissolves in acids, forming a mixture of U(IV) and U(VI) salts.

3.3 $\underline{UO_3 \text{ Hydrates}}$. The tendency for hydrate formation increases with the valency of the cation. The UO_3 hydrates are much more stable and therefore better known than the hydrates of UO_2 and U_3O_8.

(a) $\underline{\text{Phase Relationships in the System } UO_3/H_2O}$. Very little is known about the UO_3-H_2O system in solution. According to de Forcrand (1913,1915) $UO_3 \cdot 2H_2O$ is slightly soluble in water (0.16 g/l at 27°C). According to Columbia observers, at room temperature $UO_3 \cdot H_2O$ slurries in water have a pH of 4.8 to 5.2, with either the rhombic or the triclinic form as the solid phase.

Several UO_3 hydrates are known in the solid state. The compounds

$UO_3 \cdot H_2O$ (=H_2UO_4) and $UO_3 \cdot 2H_2O$ (=H_4UO_5) are well known from chemical studies. Hüttig and v. Schroeder (1922) deduced from measurements of the hydration isobar the existence of a "semi-hydrate" $2UO_3 \cdot H_2O$ (=$H_2U_2O_7$), and the possible existence of a "sesqui-hydrate," $2UO_3 \cdot 3H_2O$ (=$H_6U_2O_9$).

Hüttig and v. Schroeder prepared anhydrous UO_3 by heating $UO_4 \cdot 2H_2O$ to 500°C (to decompose all nitrate which may remain from the preparation of the peroxide from uranyl nitrate). The trioxide was completely dehydrated in vacuum at 450°C (no oxygen was lost under these conditions, cf. p. 78) and equilibrated with water vapor at room temperature. The hydration occurred with marked evolution of heat and slight increase in volume and resulted at 30°C in the formation of the dihydrate $UO_3 \cdot 2H_2O$. This dihydrate was dehydrated by heating under constant H_2O pressure of about 14 mm. Fig. 9 shows the results. The first half-mole H_2O was lost gradually between 30°C and 100°C; a second half-mole was lost suddenly at 100°C, a third half-mole, again gradually, between 100°C and 300°C, and the last half-mole suddenly at 300°C. Following the course of the isobar, from right to left, one first finds evidence of two stoichiometrically pure compounds, UO_3 and $UO_3 \cdot \frac{1}{2}H_2O$, with no mixed crystal formation between them. Then follows a region of mixed crystals, $UO_3 \cdot \frac{1}{2}H_2O + UO_3 \cdot H_2O$. It is not quite clear from the curve whether between $1H_2O$ and $2H_2O$ there is another continuous region of mixed crystallization, $UO_3 \cdot H_2O + UO_3 \cdot 2H_2O$, or whether no mixed crystals are formed in the region between $UO_3 \cdot H_2O$ and $UO_3 \cdot 1\frac{1}{2}H_2O$. If the latter is the correct interpretation, then $UO_3 \cdot 1\frac{1}{2}H_2O$ can be considered as another pure hydrate, with a region of mixed crystals extending from $UO_3 \cdot 1\frac{1}{2}H_2O$ to $UO_3 \cdot 2H_2O$.

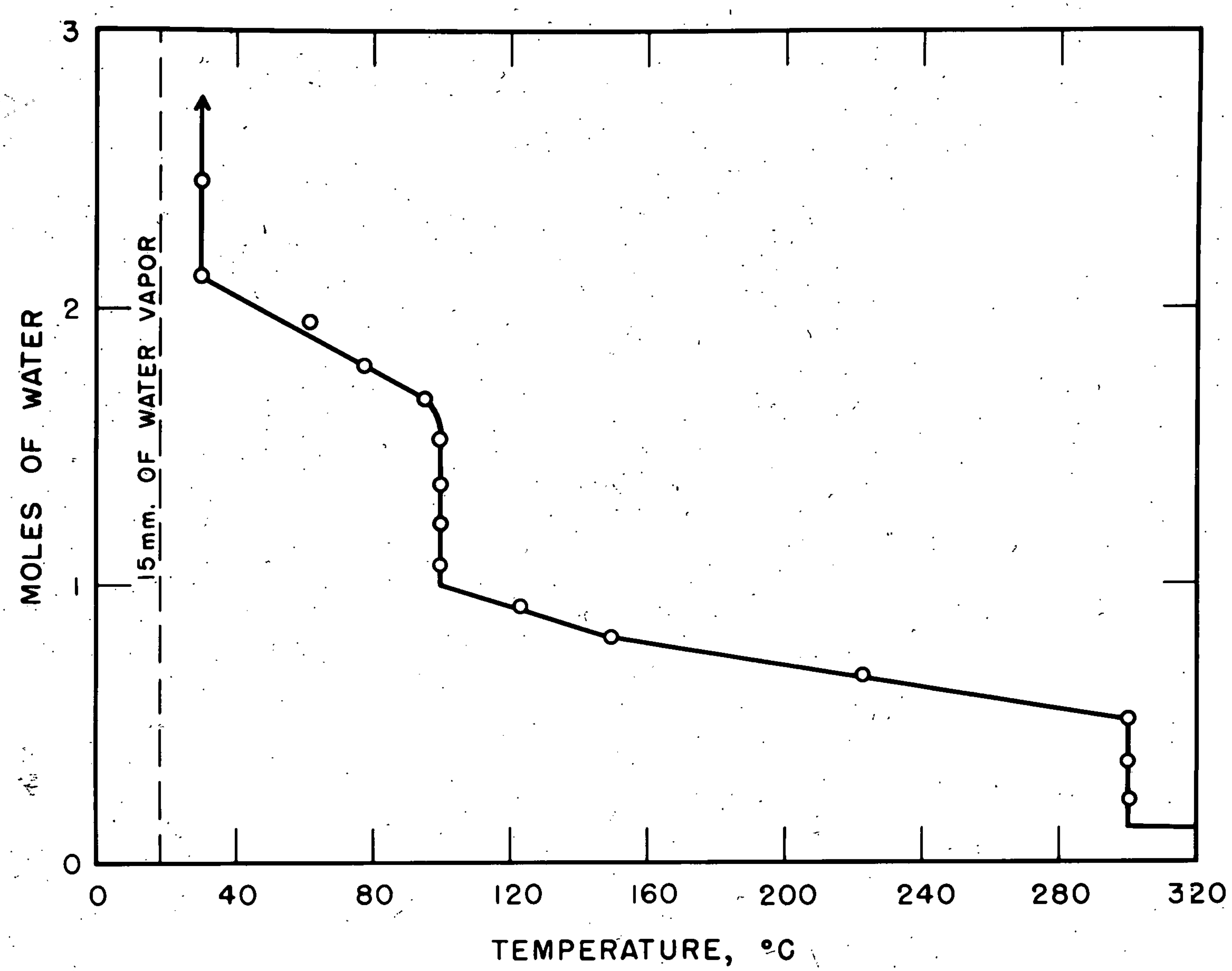

FIG. 9. THERMAL DECOMPOSITION OF $UO_3 \cdot XH_2O$ AT A PARTIAL PRESSURE OF 15mm. OF WATER VAPOR. (FROM G. HÜTTIG AND E. v. SCHROEDER, Z. ANORG. ALLGEM. CHEM., 121, 251 (1922)).

(b) Thermodynamic Properties of UO_3 Hydrates. Hüttig (1922) used the tensimetric data shown in Fig. 9 for the calculation of the heats of hydration by means of Nernst's approximation formula. His results are compared in Table 23 with the values obtained by de Forcrand (1913, 1915) from calorimetric measurements of the heats of neutralization of the oxides UO_3, $UO_3 \cdot H_2O$ and $UO_3 \cdot 2H_2O$ with diluted HNO_3 (cf. p. 133).

TABLE 24

HEATS OF HYDRATION OF UO_3

Reaction	$-\Delta H$ in kcal/mole	
	Hüttig	de Forcrand
(10) $UO_3 + \frac{1}{2}H_2O$ (gas) = $UO_3 \cdot \frac{1}{2}H_2O$	13.3	--
(11) $UO_3 + H_2O$ (gas) = $UO_3 \cdot H_2O$	23.4	15.5
(12) $UO_3 + 1\frac{1}{2}H_2O$ (gas) = $UO_3 \cdot 1\frac{1}{2}H_2O$	31.7	--
(13) $UO_3 + 2H_2O$ (gas) = $UO_3 \cdot 2H_2O$	39.2	28.5

The heats of neutralization of UO_3 hydrates by alkalis or acids leading to the formation of uranates or uranyl salts will be discussed in section 6.2 .

Pierlé (1919) measured the potential of a platinum electrode covered with $UO_3 \cdot H_2O$ gelatine paste. For results see p. 79 .

(c) Physical Properties of UO_3 Hydrates.

Crystal Structure and Habitus of $UO_3 \cdot \frac{1}{2}H_2O$. According to Columbia University observers (SAM Columbia 1,7) this hydrate forms monoclinic orange needles 5-15μ thick and 20-80μ long, with a distinct x-ray pattern of their own. Characteristic is their tendency for basal cleavage.

$UO_3 \cdot H_2O$. The monohydrate is yellow or orange-yellow. Columbia observers (SAM Columbia 1,7) distinguish an amorphous and four allotropic crystalline modifications, all stable at room temperature. These four modifications were described as follows:

(α) Large six sided orthorhombic basal tablets,

(β) Microscopic orthorhombic prismatic tablets (up to 50-100 μ), with slightly larger unit cell than in the α-modification.

Zachariasen (MP Chicago 6) gave the following more precise data for an orthorhombic form of $UO_3 \cdot H_2O$:

$a = 6.86 \pm 0.03A$; $b = 4.27 \pm 0.03A$; $c = 10.19 \pm 0.06A$.

The unit cell contains four $UO_3 \cdot H_2O$ molecules. The uranium atoms are in positions (000) ($\frac{1}{2}\frac{1}{2}0$) ($\frac{1}{2}0\frac{1}{2}$) ($0\frac{1}{2}\frac{1}{2}$). The calculated density is 6.73.

(γ) Hexagonal columnar crystals, also of microscopic size with an x-ray pattern similar to that of the α and β form, but perhaps belonging to a different system. Analysis of this form showed < 0.9 mole H_2O per mole.

(δ) Triclinic, with a complex x-ray diffraction pattern (this modification may be due to impurities). About conditions under which these four forms are obtained, see p. 60 .

In earlier investigations $UO_3 \cdot H_2O$ was described as occurring in an "amorphous" and a "rhombic" form (Aloy, 1900, 1901a and Lebeau, 1912). Riban (1881,1882) obtained $UO_3 \cdot H_2O$ in the form of hexagonal prisms by hydrolysis of uranyl acetate, Zehenter (1900), by the same method in the form of brilliant hexagonal platelets. Ipatiev and Muromtsev (1930) obtained $UO_3 \cdot H_2O$ as transparent prisms with pointed faces by hydrolysis of uranyl nitrate under high hydrogen pressure. Lebeau (1900,1901) converted amorphous $UO_3 \cdot H_2O$ into rhombic lamellae by dissolving it in uranyl nitrate solution (see p. 59), evaporating to dryness at 100°C and extracting with ether.

$UO_3 \cdot 2H_2O$. According to Columbia University observers (SAM Columbia 1,7) this yellow or greenish-yellow hydrate occurs in two modifications. Form α, obtained only as submicroscopic crystals with a simple diffraction pattern, may be face-centered tetragonal. Modification β, also known so far only in the form of submicroscopic crystals, probably is orthorhombic. Remarkably enough, the diffraction pattern of the β form of the dihydrate is identical with that of the β form of the monohydrate, the unit cell dimensions differing by less than 0.5 per cent. This may mean that the second water molecule is "zeolitic" water.

Mechanical Properties. Table 25 gives density values for UO_3 hydrates, mainly according to Kirshenbaum (SAM Columbia 3).

TABLE 25

DENSITIES OF $UO_3 \cdot xH_2O$ (after Kirshenbaum)

Compounds $UO_3 \cdot xH_2O$	x	Particle size μ	ρ (degassed) g/cc
$UO_3 \cdot \frac{1}{2}H_2O$	0.47	$< 10^5$	6.47
$UO_3 \cdot H_2O$ amorphous	1.04	44-74	6.32°
$UO_3 \cdot H_2O$ rhombic* (β)	0.82	0-10	6.07
" " " (α)		--	6.73**
" " triclinic (δ)	1.00	<105	5.74
" " " "	1.00	1-2	5.85
$UO_3 \cdot 2H_2O$	2.12	--	4.87

° Malaguti (1843) gave 5.93 g/cc.
* 1 per cent UO_4.
** Zachariasen (MP Chicago 6) x-ray density.

Columbia observers (SAM Columbia 4) found that the scratch hardness of UO_3 hydrates up to $UO_3 \cdot 2\ H_2O$ is 2.5 on Moh's scale.

Optical Properties. Color. $UO_3 \cdot \frac{1}{2}H_2O$ has been described as orange, $UO_3 \cdot H_2O$ as orange-yellow or yellow and $UO_3 \cdot 2H_2O$ as pure yellow or greenish-yellow.

Fluorescence. Anhydrous UO_3 is non-fluorescent, even at 196°C (and the same is true of UO_2, U_3O_8 and $UO_4 \cdot 2H_2O$). All UO_3 hydrates, on the other hand, fluoresce at room temperature and below. The general structure of the fluorescence spectrum is not unlike that of the uranyl ion, but the bands lie further towards the red and are limited to a more narrow region (500-600 $m\mu$). The fluorescence light is green rather than greenish-yellow, as in the case of uranyl salts. The fluorescence spectra of $UO_3 \cdot 2H_2O$ (α and β), $UO_3 \cdot H_2O$ (α, β, and δ) and $UO_3 \cdot \frac{1}{2}H_2O$ were examined at Columbia University (SAM Columbia 8) and found to be similar but easily distinguishable. Each contains 3-4 bands at intervals of about 810 cm^{-1}. The first two bands are strong, the third and the fourth increasingly weak. The fluorescence of UO_3 hydrates will be discussed in more detail in the second volume of this treatise, the chapter dealing with fluorescence and photochemistry of uranyl compounds.

(d) Hydration and Dehydration of UO_3. The hydration isobar shown in Fig. 9 gives information on the conditions under which the different hydrates can be expected to be formed and to decompose in contact with water vapor under 15 mm. partial pressure. Numerous additional data on equilibrium conditions and rates of hydration and dehydration are available in the Manhattan Project literature.

$UO_3\cdot 2H_2O$. This hydrate is stable at room temperature. According to early Columbia observations (SAM Columbia 4) it is formed from red-orange "active" UO_3 by action of saturated water vapor between 5°C and 75°C. Later at the same laboratory (SAM Columbia 7) the α form was obtained by hydration of amorphous UO_3 (prepared by decomposition of $UO_4\cdot 2H_2O$), and the β form by hydration of Mallinckrodt's product which is microcrystalline UO_3(III). (Cf. .)

At Berkeley (UCRL 4) it was observed that orange or brick-red UO_3 (formed by thermal decomposition of $(NH_4)_2U_2O_7$), exposed to air, is converted in several days into a yellow-green hydrate, presumably $UO_3\cdot 2H_2O$. Upon heating this hydrate is quickly reconverted into the brick-red anhydrous oxide.

De Forcrand (1913,1915) found that direct hydration of UO_3 easily leads to products containing as much as 2.5 H_2O, and that dehydration of these products is likely to go beyond the stage of $2H_2O$, so that the stoichiometric composition $UO_2\cdot 2H_2O$ can be obtained only by interrupting the dehydration at the right moment.

Instead of hydration by water vapor $UO_3\cdot 2H_2O$ can also be obtained by the action of liquid water on UO_3 or $UO_3\cdot H_2O$. Lebeau (1912) prepared the dihydrate by dissolving $UO_3\cdot H_2O$ in concentrated aqueous solution of uranyl nitrate (cf. p. 56), evaporating over sulfuric acid at room temperature and removing the uranyl nitrate by ether extraction. The residue was a light yellow powder with the composition $UO_3\cdot 2H_2O$. The upper limit of stability of $UO_3\cdot 2H_2O$ in contact with liquid water is considerably below 100°C, more exactly, at 75°C according to the first Columbia University observations (SAM Columbia 4), or at 60°C according to the more recent data (SAM Columbia 7). The fact that the water vapor pressure over

$UO_3 \cdot 2H_2O$ is higher than over H_2O at temperatures above approximately 60°C was confirmed by direct measurements at 61°C and 77°C.

The figures in Table 26 characterize the rate of dehydration of $UO_3 \cdot 2H_2O$ at different temperatures:

TABLE 26

RATE OF DEHYDRATION OF $UO_3 \cdot 2H_2O$

Preparation	Time required for loss of one molecule H_2O (minutes)					
	28°C (in vac.)	61°C	77°C	87°C	103°C	118°C
		(in water vapor)				
$UO_3 \cdot 2H_2O$ from UO_4	--	>518	<95	>12	<2	<1
$UO_3 \cdot 2H_2O$ from Mallinckrodt UO_3	<123	>100	<122; >48	<2	--	--

Earlier, de Forcrand (1913) had stated that $UO_3 \cdot 2H_2O$ loses H_2O slowly over H_2SO_4 at room temperature, is rapidly dehydrated to $UO_3 \cdot H_2O$ in a stream of dry air at 80°C and boils at about 135°C; Lebeau (1912) reported that $UO_3 \cdot 2H_2O$ is converted to $UO_3 \cdot H_2O$ by boiling in water. Drenckman (1861), on the other hand, had asserted that conversion to monohydrate occurs only at 160°C.

$\underline{UO_3 \cdot H_2O}$. Heating $UO_3 \cdot 2H_2O$ above 60°C must lead, according to Fig. 9, first to the formation of mixed crystals of dihydrate and monohydrate (or of dihydrate and sesquihydrate); conversion to pure monohydrate $UO_3 \cdot H_2O$ should require, according to this figure, heating to about 100°C (under 15 mm H_2O pressure). A still higher temperature should be necessary under water or in contact with saturated water vapor. The formation of mixed crystals was not taken into account at Columbia University (SAM Columbia 4) and the limits of stability of the monohydrate in contact with water were given first (SAM Columbia 7) as 85°C-300°C for the rhombic form and 300°C-310°C for the triclinic form. In the same paper "active" red-orange UO_3 was stated to be converted into rhombic $UO_3 \cdot H_2O$ by exposure to saturated water vapor at 85°C-300°C, and to triclinic $UO_3 \cdot H_2O$ at $> 300°C$; while "inactive" orange-yellow UO_3 was stated to require for hydration a temperature of 150°C-300°C and to give triclinic $UO_3 \cdot H_2O$ plates.

In a subsequent investigation at Columbia University (SAM Columbia 7) the yellow orthorhombic α form of $UO_3 \cdot H_2O$ was obtained directly from $UO_4 \cdot H_2O$ by heating in water to 158°C for one hundred and seventeen hours, as well as by heating the β form of $UO_3 \cdot 2H_2O$ in water to 100°C for one hundred to six hundred hours.

The orange β form of the monohydrate was obtained from the α or β dihydrate by heating to 100°C for ninety hours. The γ form of $UO_3 \cdot H_2O$ was obtained by heating $UO_4 \cdot 2H_2O$ or $UO_3 \cdot 2H_2O$ in water to 185°C-310°C. Finally, the δ form of the monohydrate was obtained by dehydration of α $UO_3 \cdot 2H_2O$ in water at 185°C-310°C.

According to the same investigation, $UO_3 \cdot H_2O$ does not change by heating in water in sealed tubes to temperatures from 60°C to 325°C. $UO_3 \cdot H_2O$ crystals do not take up more H_2O after a month in water at 28°C (although $UO_3 \cdot 2H_2O$ is the stable hydrate under water up to 60°C). All four crystallographic forms are very stable at low temperatures; qualitative vapor pressure observations indicate that the hexagonal form is the most stable below 125°C, the rhombic form between 125°C and 300°C, and the triclinic form at 300°C-310°C. $UO_3 \cdot H_2O$ loses 85 per cent of its water in three hours at 400°C and > 95 per cent in one hour at 450°C.

The following earlier observations can also be quoted here: $UO_3 \cdot H_2O$ loses no water in vacuum or dry air at 100°C (Aloy, 1900, 1901a); loses

5 per cent of its water in thirty minutes at 300°C, 50 per cent at 400°C, 94 per cent at 500°C (Lebeau, 1912); boils at about 220°C (de Forcrand, 1913); is transformed into anhydrous UO_3 at 300°C and into U_3O_8 at red heat (Ebelmen, 1842b).

Lebeau (1912) obtained $UO_3 \cdot H_2O$ by hydration of UO_3 in air at 25°C (in twenty-four hours) and at 100°C (in one hour) apparently as intermediate in the conversion of UO_3 to $UO_3 \cdot 2H_2O$. At the Metallurgical Laboratory (SAM Columbia 9) the growth of hexagonal and plate-like crystals (apparently of $UO_3 \cdot H_2O$?) was observed after thirty minutes of digestion of a suspension of UO_3 in water at 100°C.

$\underline{UO_3 \cdot \frac{1}{2}H_2O}$. According to Hüttig and v. Schroeder (1922) (cf. Fig. 9) the semihydrate can be obtained under 15 mm H_2O pressure, between 160°C and 300°C. At Columbia University (SAM Columbia 7) the semihydrate was prepared by heating $UO_4 \cdot 2H_2O$ in water to 310°C-350°C as well as by hydrating "inactive" orange-yellow UO_3 at 350°C-380°C (SAM Columbia 4). It is stable in sealed tubes under water > 325°C, is slowly hydrated to $UO_3 \cdot H_2O$ < 300°C (hydration is complete in twenty hours at 100°C). According to the same laboratory (SAM Columbia 6) the water content is reduced from 2.8 per cent to 0.5 per cent of total weight in four hours at 450°C in air in an open dish; heating to 500°C-550°C removes all water. The semihydrate is converted to red UO_3 (containing some U_3O_8) by heating to 450°C-600°C in air, and to pure U_3O_8 by heating to 700°C (SAM Columbia 4).

3.4 $\underline{UO_4 \text{ Hydrates}}$.

(a) $\underline{\text{Dehydration of } UO_4 \cdot aq}$. Uranium peroxide, UO_4, has not been obtained in the pure anhydrous state. When dehydrated, it loses oxygen simultaneously with water until it is converted to UO_3 (or lower oxides, depending on temperature and duration of dehydration). This was first established by Alibegoff (1886) and confirmed by experiments of Hüttig and v. Schroeder (1922) and Rosenheim and Daehr (1929).

The study of the UO_4/H_2O system is complicated by this simultaneous loss of water and oxygen. Systematic measurements of the dehydration equilibrium as such should be made under oxygen pressures high enough to prevent deoxygenation as far as possible.

Freshly precipitated, air-dried uranium peroxide may contain as much as four or more molecules water per atom uranium. Fairley (1877) ascribed to air-dried $UO_4 \cdot aq$ the composition $UO_4 \cdot 4H_2O$. Rosenheim and Daehr (1929) found that air-dried $UO_4 \cdot aq$ contains three molecules water. Hüttig and v. Schroeder (1922) found about four and one-half molecules H_2O in peroxide dried in air at 35°C. At the Metallurgical Laboratory (SAM Columbia 10) air-dried uranium peroxide (precipitated from uranyl nitrate at 75°C by 3 per cent H_2O_2) was found to contain $4H_2O$ (see, however, the discussion of x-ray analysis on p. 66).

At Berkeley (MP Berkeley 2), on the other hand, the following analytical results were obtained with air-dried peroxide preparations:

Washed with water, alcohol and ether: $UO_{3.98} \cdot 2.11\ H_2O$

Washed with water only: $UO_{3.96} \cdot 2.18\ H_2O$

Hüttig and v. Schroeder (1922) studied the dehydration of $UO_4 \cdot aq$ under constant H_2O pressure ($\sim$ 15 mm) in the same way as that of $UO_3 \cdot aq$ (cf. p. 54). Fig. 10 shows the dehydration and deoxygenation isobars obtained in this study. They started with air-dried preparations which contained about four and one-half molecules H_2O per atom uranium. (This

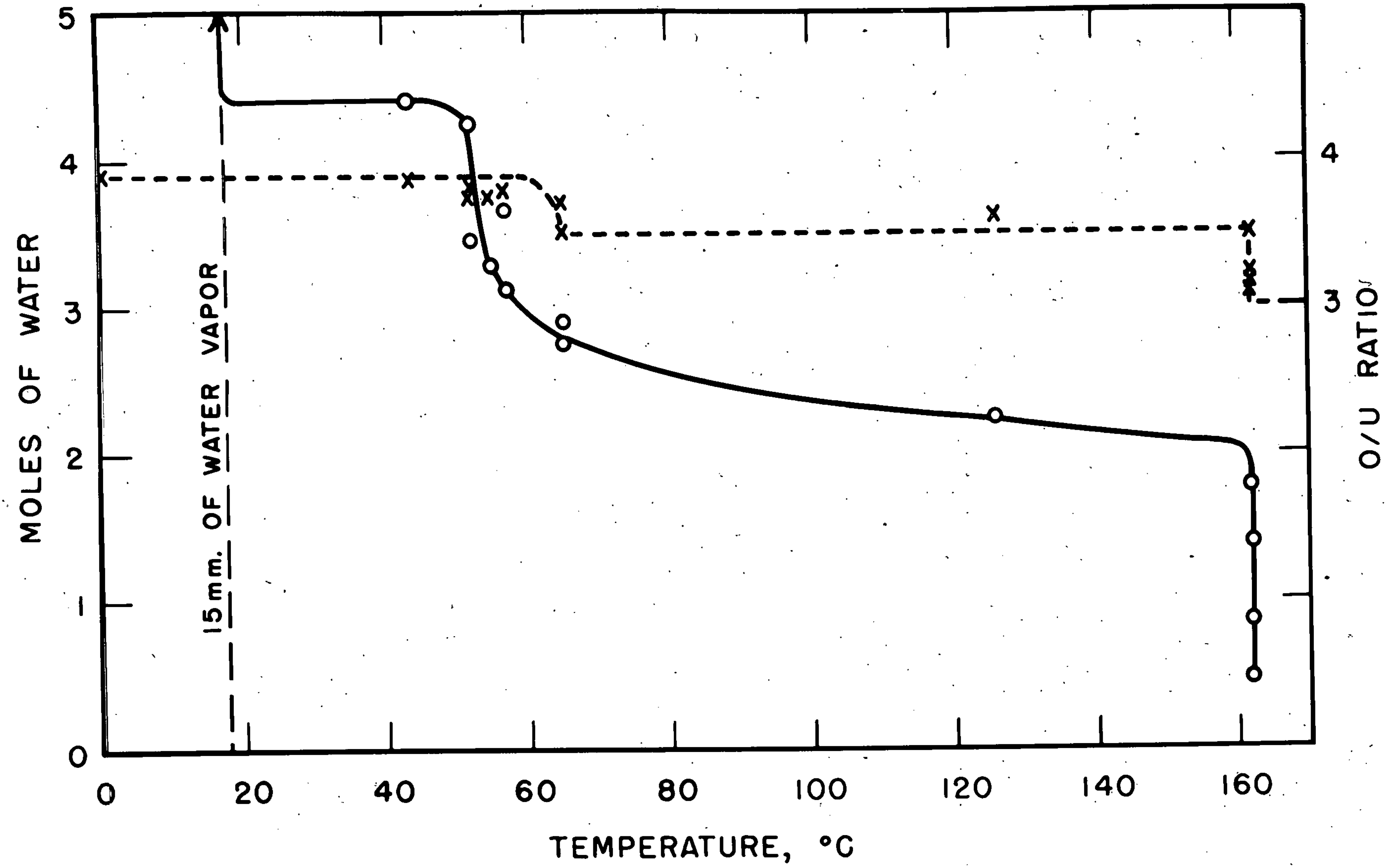

FIG. 10. THERMAL DECOMPOSITION OF $UO_4 \cdot XH_2O$ AT A PARTIAL PRESSURE OF 15mm. OF WATER VAPOR. (FROM G. HÜTTIG AND E. v. SCHROEDER, Z. ANORG. ALLGEM. CHEM., 121, 247 (1922)).

phase was interpreted by Hüttig as an addition compound of H_2O_2, H_2O and UO_3: $UO_3 \cdot H_2O_2 \cdot 3\frac{1}{2}H_2O$.) Curves show that one half of the peroxide oxygen is lost as early as at 54°C when the compound still contains three and one-half molecules of water. The resulting phase, $UO_{3.5} \cdot 3H_2O$, was interpreted by Hüttig as $UO_3 \cdot \frac{1}{2}H_2O_2 \cdot 2\frac{1}{2}\ H_2O$. Between 54°C and 163°C another molecule of water is lost gradually until the composition $UO_{3.5} \cdot 2H_2O$ is reached (according to Hüttig, $UO_3 \cdot \frac{1}{2}H_2O_2 \cdot 1\frac{1}{2}H_2O$). This may correspond to a separate compound or to mixed crystals of $UO_{3.5} \cdot 3H_2O$ and $UO_3 \cdot 1\frac{1}{2}H_2O$. At 163°C the remaining peroxide oxygen is lost together with one and one-half molecules of water, leaving $UO_3 \cdot \frac{1}{2}H_2O$ as the solid phase. The last half-mole water was found in these experiments to be lost somewhere near 450°C. This agrees with the results of experiments on the dehydration of $UO_3 \cdot 2H_2O$ (described in Section 3.3(d)).

Hüttig denied the existence of an oxide UO_4 and interpreted the "UO_4 hydrates" as loose addition compounds of UO_3, H_2O_2 and H_2O. However, this interpretation does not follow necessarily from his observations.

It will be noted that, according to Fig. 10, one-half atom of peroxide oxygen is lost before the water content has decreased to $2H_2O$; in other words a compound $UO_4 \cdot 2H_2O$ ($=UO_3 \cdot H_2O_2 \cdot H_2O$) does not exist, according to Hüttig, under 15 mm H_2O pressure. This conclusion appears to be in disagreement with the observations of many other investigators who found $UO_4 \cdot 2H_2O$ the most stable form of uranium peroxide.

Fairley (1877) gave $UO_4 \cdot 2H_2O$ as the composition of uranium peroxide dried at 100°C. This was confirmed by Alibegoff (1886) and by Rosenheim and Daehr (1929a, 1932).

At Brown University (Brown 3) it was observed that drying $UO_4 \cdot aq$ (precipitated at 75°C) at 30°C [illegible] a [illegible] which is in excess of that required by the formula $UO_4 \cdot 2H_2O$; further dehydration is very slow up to 125°C (where H_2O and O_2 begin to escape simultaneously). At 60°C-70°C, $UO_4 \cdot 2H_2O$ can be dried for thirteen hours without appreciable loss of oxygen (Brown 4).

According to Columbia University observations (SAM Columbia 10) the peroxide prepared by Kraus' method, which had the composition $UO_4 \cdot 4H_2O$ after drying in open air, was converted to $UO_4 \cdot 2H_2O$ by drying at 100°C in air, or at room temperature over 36 N H_2SO_4.

According to Columbia University observations (SAM Columbia 11) the peroxide prepared at 75°C and dried in oxygen for three hours at 37°C and for three hours at 62°C also has the composition $UO_4 \cdot 2H_2O$. The water content was found unchanged after further three hours in air at 85°C, or three hours in oxygen at 105°C, or thirteen hours in oxygen at 75°C. Oxygen started to escape slowly a little below 100°C. (For details of UO_4 conversion to lower oxides, see Section 4.6(c), p. 106.)

Heat of Formation of $UO_4 \cdot 2H_2O$. Pissarjevsky (1900) measured the heats of reaction of $UO_4 \cdot 2H_2O$ (dried at 100°C) and of $UO_3 \cdot H_2O$ (method of preparation not given) with 2 N H_2SO_4. The first reaction was assumed to give uranyl sulfate and H_2O_2, the second one, uranyl sulfate and H_2O. Using the known heat of oxidation of H_2O to H_2O_2, Pissarjevsky calculated the heat of formation of $UO_4 \cdot 2H_2O$ from $UO_3 \cdot H_2O$, O_2 and H_2O:

(14) $UO_4 \cdot 2H_2O = UO_3 \cdot H_2O + \frac{1}{2}O_2 + H_2O + 6.15$ kcal.

(b) Physical Properties of UO_4 Hydrates. Density of $UO_4 \cdot 2H_2O$ (DuPont product, 79 per cent UO_4, 11 per cent H_2O, 10 per cent UO_3) was found at Columbia University (SAM Columbia 3) to be 4.31 g/cc (degassed). Bulk density of dried $UO_4 \cdot 2H_2O$ not tapped, 0.72; tapped, 1.00 g/cc according to Berkeley observations (UCRL 1).

Crystal Structure. $UO_4 \cdot 2H_2O$ has usually been described as "amorphous". Rosenheim and Daehr (1929) found that a crystalline peroxide can be prepared by adding an equal volume of 30 per cent H_2O_2 to a 14 per cent solution of ammonium uranyl oxalate at room temperature and heating the gelatinous precipitate with twice its volume of water almost to the boiling point. This leads to a dark yellow solution from which fine needle-like crystals are formed upon slow cooling. These were found to have a composition $UO_4 \cdot 3H_2O$ and to be converted to $UO_4 \cdot 2H_2O$ by drying in air at 100°C, or in vacuum over P_2O_5 at room temperature. However, attempts to repeat the preparation of this "crystalline peroxide" at Berkeley (MP Berkeley 2) gave a compound containing NH_4^+ and oxalate, presumably $UO_4 \cdot \frac{1}{2}(NH_4)_2C_2O_4 \cdot 1\frac{1}{2}$-$2\ H_2O$. This may also have been Rosenheim and Daehr's product. According to Columbia University (SAM Columbia 7,12) $UO_4 \cdot aq$, precipitated by addition of one liter 3 per cent H_2O_2 to 210 g uranyl nitrate in one liter H_2O at 75°C, was microcrystalline and showed a diffuse x-ray pattern. At the Metallurgical Laboratory (MP Chicago 2,6) an air-dried sample of $UO_4 \cdot aq$ which allegedly contained $4H_2O$ (cf. p. 63) was studied by x-rays. The lines were diffuse, indicating a crystallite size of 100-200A. The unit cell was found to be orthorhombic, face centered with the parameters

$$a_1 = 8.74 \pm 0.05A; \qquad a_2 = 6.50 \pm 0.03A \quad \text{and} \qquad a_3 = 4.21 \pm 0.2A.$$

The two uranium atoms in the unit are situated in positions (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. Zachariasen pointed out that this structure seems to offer insufficient space for four water molecules. The densities calculated for different possible water contents were

Composition	ρ g/cc
$UO_4 \cdot 4H_2O$	5.15
$UO_4 \cdot 3H_2O$	4.90
$UO_4 \cdot 2H_2O$	4.66

Hardness. Scratch hardness: Mohs 2.5; if wet and fluffy, Mohs 2, according to Columbia University observers (SAM Columbia 4).

Paramagnetism. Tilk and Klemm (1939) measured the paramagnetism of $UO_4 \cdot xH_2O$ and found χ (specific, calculated for anhydrous oxide) $= 0.17 \times 10^{-6}$, χ (molar) $= 51 \times 10^{-6}$, χ (molar, corrected for diamagnetism) $= 111 \times 10^{-6}$. (The values used for U^{6+} and O^{--} respectively in applying the correction for diamagnetism were -11.25×10^{-6} and -20×10^{-6}.) The paramagnetism is independent of temperature.

Optical Properties. $UO_4 \cdot aq$ is faintly yellow in color. In contrast to $UO_3 \cdot aq$ it does not fluoresce either at room temperature or at the temperature of liquid nitrogen (SAM Columbia 1,8).

3.5 Uranium Oxide Hydrosols and Suspensions.

(a) Uranium Oxide Hydrosols.

UO_2 Hydrosol. Samsonov (1911) obtained a black precipitate by electrolytic reduction of a solution of 50 g uranyl chloride in 100 cc of 2 N HCl; this precipitate easily formed a hydrosol. The hydrosol was very unstable and coagulated after standing about twenty-four hours. Its stability could be increased by the addition of uranium tetrachloride. The particles are visible in the ultramicroscope. They carry out a lively Brownian motion and carry a positive charge, as shown by their movement in an electric field and by their coagulation by anions. The hydrosol contains up to

0.2 mole UO_2 per liter. A similar hydrosol can also be prepared by reduction of UO_2Cl_2 with zinc or copper in dilute hydrochloric acid.

$\underline{UO_3}$ Hydrosol. A uranium trioxide hydrosol was first prepared by Graham (1862) by precipitation with KOH from uranyl nitrate (or chloride) solution in the presence of sugar, and subsequent dialysis. The orange-yellow hydrosol, completely free of acid or alkali, is very stable. It can be coagulated by salts and re-peptized by water.

Mylius and Dietz (1901) obtained colloidal UO_3 from a precipitate obtained by hydrolysis of UO_2Cl_2 with silver oxide. The yellow, weakly acid colloid (it contains some hydrochloric acid which cannot be removed by dialysis) is stable at 0°C but decomposes at room temperature with precipitation of $UO_3 \cdot 2H_2O$.

Szilard (1907) decomposed a solution of uranyl acetate in water-ether mixture by exposure to light. The violet $U_3O_8 \cdot xH_2O$ precipitate was allowed to oxidize in air to a yellow UO_3 hydrate. The latter was suspended in water and the suspension gradually added to hot diluted uranyl nitrate (or thorium nitrate) solution, producing a very stable hydrosol (orange-yellow with uranyl nitrate, greenish-yellow with thorium nitrate).

Sen (1928) studied the effect of different sugars on the peptization of UO_3 hydrate. The precipitation of UO_3 hydrate by alkali can be prevented by the presence of sucrose, lactose, glucose or fructose.

Kargin(1931) found that a UO_3 hydrosol can be obtained simply by precipitating ammonium diuranate from uranyl nitrate solution by ammonia with stirring and peptizing in a large volume of water.

Diachkovski (1926,1931) precipitated alkali uranate from UO_2Cl_2 solution with 0.1 N alkali hydroxide; the precipitate was washed with hot water until it began passing through the filter, and peptized in a

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large volume of water. Alkali was removed by dialysis. The sol particles were negatively charged; they had a size of about 5×10^{-5} cm and a density of 7.45 g/cc. The sol could be coagulated by KCl and $BaCl_2$, and its charge was reversed by $AlCl_3$. At 15°C the viscosity of the sol at 15 per cent was 1.0393 that of water. The hydrosol was stable to boiling but coagulated on freezing. The surface tension of the 1 per cent sol showed a maximum at 30°C-40°C.

(b) Uranium Oxide Suspensions. Aqueous suspensions of various uranium oxides have been studied at Columbia University. Table 25 is from the summary report of this laboratory (SAM Columbia 1). It shows how heavy these "slurries" can be made without losing fluidity.

The properties of the UO_2 slurry do not change after several days at 200°C.

TABLE 27

MAXIMUM URANIUM DENSITY IN FLUID OXIDE SLURRIES

Oxide	g U/cc	ρ g/cc	Apparent oxide density in water g/cc	Per cent oxide by weight	Per cent oxide by volume	Particle size, mesh
UO_2	3.5	4.6	9.8	87	40	<100
U_3O_8	2.5	3.6	7.0	83	42	<140
$UO_3 \cdot \frac{1}{2}H_2O$	2.3	3.4	6.5	84	44	200-325
$UO_3 \cdot H_2O$ triclinic	2.0	3.1	5.6	82	46	<140
$UO_3 \cdot H_2O$ amorphous	1.9	3.0	6.0	81	41	200-325
UO_4 with 24% H_2O	0.12*	1.13	4.3	15	4	≈10 µ

* Creamy, gelatinous; stiffens above 1.3 g U/cc.

4. Oxidation and Reduction of Uranium and Its Oxides

4. OXIDATION AND REDUCTION OF URANIUM AND ITS OXIDES

4.1 Thermodynamics of Formation and Interconversion of Uranium Oxides.

(a) Heats of Formation and Interconversion. Direct calorimetric data were obtained by Mixter (1912) for the combustion of uranium and UO_2 to U_3O_8 and for the formation of sodium uranate (Na_2UO_4), from uranium, UO_2, U_3O_8, or UO_3 and sodium peroxide (see p. 129). The heats of formation of UO_2 and U_3O_8 could therefore be calculated either from combustion with oxygen or from the reaction with Na_2O_2, whereas the heat of formation of UO_3 could be derived only from experiments with Na_2O_2. An independent calculation of the heat of formation of UO_3 was made by Biltz and Fendius (1928). These investigators compared the heat of formation of uranyl chloride solutions from UCl_3 (or UCl_4) with the heat of formation of the same solutions from UO_3 and also measured directly the heats of formation of UCl_3 and UCl_4 from the elements (cf. p. 72). Their results were critically reviewed and corrected at the UCRL (UCRL 2). The results of the two calorimetric investigations are shown in Table 28.

Biltz and Müller (1927) made estimates of the heats of reaction (18) and (20) (Table 28) from the decomposition pressures of the oxides UO_3 and U_3O_8. Somewhat more detailed calculations were made, using the same experimental data, by Brewer (MP Berkeley 1). The tensimetric data of Biltz and Müller are insufficient for exact calculation because of the formation of solid solutions. To obtain exact results the Van't Hoff equation would have to be applied not only to the decomposition isochores of U_3O_8 and UO_3, but also to those of all the oxides of intermediate compositions, and the total heat of oxygenation would have to be obtained by

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integration of the "differential" heats (as derived from this equation) over the ranges x = 2.0 to 2.67 and x = 2.67 to 3.0, respectively.

TABLE 28

HEATS OF FORMATION OF URANIUM OXIDES (PER G ATOM URANIUM)

Reaction	Calorimetric data kcal/g atom U				Brewer (MP Berkeley 1) *
	Mixter (1912)		Biltz and Fendius (1928)		
	Combustion	Reaction with Na_2O_2	via UCl_3	via UCl_4	
(15) $U + O_2 \rightarrow UO_2$	256.6	269.7**	--	--	(257)
(16) $U + 8/3\ O_2 \rightarrow 1/3\ U_3O_8$	281.7	293.5	--	--	285
(17) $U + 3/2\ O_2 \rightarrow UO_3$	--	303.9	294	292 288^{+}	291
(18) $UO_2 + 1/3\ O_2 \rightarrow 1/3\ U_3O_8$	25.1	28.8	--	--	28
(19) $UO_2 + \frac{1}{2}O_2 \rightarrow UO_3$	--	34.2	$(27)^{x}$	$(25)^{x}$	34
(20) $1/3\ U_3O_8 + 1/6\ O_2 \rightarrow UO_3$		5.4	$(12)^{x}$	$(10)^{x}$	6

* Calculated from Biltz and Müller's tensimetric data; cf. below for details of calculation.

+ Corrected by MacWood and Altman (UCRL 2).

x By combination with Mixter's combustion values.

** MacWood (UCRL 3) has recalculated Mixter's value using better data for Na_2O_2 and Na_2O and gives $\Delta H = -270.4$ kcal/mole.

No attempts at such exact calculation were made. In the range between U_3O_8 and UO_3, Biltz and Müller applied the Van't Hoff equation to "average" pressure values obtained by a rather arbitrary averaging process from the isothermals at 500°C, 530°C and 610°C (cf. Fig. 6). They calculated in this way an "average decomposition heat" of 17 kcal/g atom oxygen or

5.67 kcal/g atom uranium, in satisfactory agreement with Mixter's value in Table 28 (5.4 kcal/g atom uranium). Brewer (MP Berkeley 1) calculated from the same data a value of 17.5 kcal/g atom oxygen.

In the range between UO_2 and U_3O_8 the Van't Hoff equation was applied by Biltz and Müller to the diphasic, constant pressure region $UO_{2.30}$ to $UO_{2.62}$ (using the temperature range 1160°C-1240°C). This led to a value $-\Delta H = 39.5$ kcal/g atom oxygen for the heat of conversion of $UO_{2.30}$ to $UO_{2.62}$. This figure is close to Mixter's value for the conversion of UO_2 to U_3O_8 in Table 26 (25-29 kcal/g atom uranium, or 37.5-43.5 kcal/g atom oxygen). Brewer (MP Berkeley 1) calculated, also from Biltz's data, $-\Delta H = 40.5$ kcal/g atom oxygen.

The "first" differential heat of oxygenation of UO_2 certainly is $\gg 40$ kcal/g atom oxygen. Brewer estimated, from the one pressure value given by Biltz for $UO_{2.20}$, that the average heat of oxygenation between $UO_{2.00}$ and $UO_{2.25}$ is approximately 48 kcal/g atom oxygen. He further estimated 30 kcal/g atom oxygen as the average heat of oxygenation between $UO_{2.62}$ and $UO_{2.67}$. The "last" differential heat of oxygenation of UO_2 to U_3O_8 was estimated by Biltz and Müller to be as low as 15 kcal/g atom oxygen.

By combining three estimates (48 kcal/g atom oxygen for the range $x = 2.00$ to 2.25; 40.5 kcal/g atom oxygen for the range $x = 2.25$ to 2.62 and 30 kcal/g atom oxygen for the range $x = 2.62$ to 2.67) with Mixter's value (257 kcal/g atom uranium) for the heat of formation of UO_2, Brewer calculated 285 kcal/g atom uranium as the heat of formation of U_3O_8; by adding 17.5 kcal/atom oxygen for the heat of oxygenation of U_3O_8 to UO_3 he obtained 291 kcal/g atom uranium as the heat of formation of UO_3. These values are given in the last column of Table 28.

The heat of formation of UO_3 must depend on the allotropic form. According to Brewer the values obtained above probably apply to the hexagonal form UO_3(I); the amorphous form may be slightly less stable while the crystalline forms UO_3(II) and UO_3(III) may be more stable than UO_3(I) by 1-2 kcal/g atom uranium.

The fact that the monoxide UO can be formed from uranium and UO_2 indicates that $-\Delta H_{UO}$ is $>$ 129 kcal/mole (one half of the heat of formation of UO_2). On the other hand, since magnesium reduces the higher uranium oxides to metal (and not to UO), $-\Delta H$ must be $<$ 142 kcal/mole. The most probable value is therefore $-\Delta H_{UO} = 135 \pm 5$ kcal.

(b) <u>Free Energies and Entropies of Formation and Interconversion</u>

<u>UO</u>. The entropy of the monoxide was given by Brewer (MP Berkeley 1) as -20 E.U. at 1000°K.

<u>UO_2</u>. Brewer (MP Berkeley 4) used Mixter's value of ΔH and an estimate of the entropy of uranium and UO_2, attributed to Latimer,

$$-\Delta S_{UO_2} = 42.1 \text{ E.U.},$$

to calculate the free energy of formation of UO_2. He obtained

$$-\Delta F_{UO_2}(298.15°K) = 244 \text{ kcal/mole}.$$

Later (MP Berkeley 1) the same author gave

$$\Delta S_{UO_2} = 42.5 \text{ at } 298°K,\ 41.9 \text{ at } 500°K,$$
$$40.5 \text{ at } 1000°K,\ 40.1 \text{ at } 1500°K.$$

The above given value of the free energy of formation of UO_2 (-244 kcal/mole) permits one to estimate that heating to 4200°K will be necessary for the equilibrium pressure of oxygen over uranium dioxide to reach 10^{-2} mm Hg.

The entropy of formation of $UO_{2.25}$ (assumed by Brewer to be the upper limit of solid solubility of oxygen in UO_2) was estimated by him as

$$\Delta S = 45.5 \text{ E.U.} \qquad (1000°K)$$

$\underline{U_3O_8}$. The tensimetric data of Biltz and Müller can be used for the calculation of free energy of formation of this oxide from UO_2 and O_2 (cf. reaction (18)). MacWood and Altman (UCRL 2) assumed, as an approximation, the constant decomposition pressures found in the range $UO_{2.30}$-$UO_{2.62}$ to be valid for the whole range $UO_{2.0}$-$UO_{3.0}$ and calculated from them the equation

$$(21) \qquad -\Delta F° = 74.432 - 2.35\ T \log T - 4.75 \times 10^{-4}\ T^2 + 3.096 \times 10^5\ T^{-1} - 28.61\ T \quad (\text{cal/mole } U_3O_8)$$

leading to

$$-\Delta F°_{298} = 65.07 \text{ kcal/mole } U_3O_8.$$

In deriving equation (21) use was made of equations (5) and (6) for the specific heats of UO_2 and U_3O_8 respectively. This gives (for the formation of one mole U_3O_8 from three moles UO_2 and one mole O_2)

$$(22) \qquad \Delta C_p = 1.02 + 9.51 \times 10^{-4}\ T - 6.193 \times 10^5\ T^{-2},$$

and hence:

$$(23) \qquad -\Delta H = 74.432 + 1.02\ T + 4.75 \times 10^{-4}\ T^2 + 6.193 \times 10^5\ T^{-1},$$

leading to

$$-\Delta H_{298} = 76.75 \text{ kcal/mole } U_3O_8.$$

By combination with the above given value of $\Delta F°_{298}$ (65.07 kcal/mole), one obtains

$$-\Delta S_{298} = 39.2 \text{ E.U.}$$

The $-\Delta H$ value used (76.8 kcal/mole U_3O_8, or 25.6 kcal/g atom uranium) is in satisfactory agreement with the values given in Table 28.

Kirshenbaum (SAM Columbia 12) gave for the same reaction

$$(24) \qquad -\Delta F^\circ = +76{,}890 - 63.1\,T + 2.58 \times 10^{-3}\,T^2 - 0.32 \times 10^{-6}\,T^3 - 0.62 \times 10^5\,T^{-1} + 3.22\,T \ln T \quad (\text{cal/mole } U_3O_8)$$

leading to the values of ΔF°_T given in Table 29.

TABLE 29

FREE ENERGY OF OXIDATION OF UO_2 to U_3O_8

$T^\circ K$	300	400	500	600	1000
$-\Delta F^\circ_T$ kcal/mole U_3O_8	63.45	59.6	55.8	52.1	38.2

Equation (24) was based on data for the reaction:

$$(25) \qquad U_3O_8 + 2H_2 \longrightarrow 3UO_2 + 2H_2O\ (g)$$

given by Burton and Davis (MP Chicago 9).

For the formation of U_3O_8 from the elements, MacWood and Altman calculated (by using Mixter's value for ΔH_{298} and the above-mentioned specific heat equations)

$$(26) \qquad -\Delta H = 850{,}000 - 19.01\,T + 9.65 \times 10^{-3}\,T^2 - 3.984 \times 10^5\,T^{-1}$$

and obtained by Nernst's approximation:

$$(27) \qquad -\Delta F^\circ = 850{,}000 + 43.79\,T \log T - 9.65 \times 10^{-3}\,T^2 + 1.992 \times 10^5\,T^{-1} - 303.1\,T,$$

leading to

$$-\Delta F^\circ_{298} = 791.7 \text{ kcal/mole } U_3O_8 \text{ and}$$

$$-\Delta S_{298} = 184.2 \text{ E.U.}$$

In Table 30 the results of MacWood and Altman are compared with the figures given by Brewer.

TABLE 30

THERMODYNAMICS OF FORMATION OF U_3O_8

	MacWood (UCRL 2)	Brewer (MP Berkeley 1)
$-\Delta H_{298}$ (kcal/mole U_3O_8)	846.6*	855**
$-\Delta F^\circ_{298}$ (kcal/mole U_3O_8)	791.7	805
$-\Delta S$ (E.U.)	184.2	166

* Mixter's value
** Derived as described on p. 73 .

Brewer also gave the following values of the function $(\Delta F_T - \Delta H_{298})/T$ for the formation of U_3O_8 from the elements:

TABLE 31

ENTROPY OF FORMATION OF U_3O_8 AT VARIOUS TEMPERATURES

T°K	298	500	1000	1500
$(\Delta F_T - \Delta H_{298})/T$ cal/°K per mole U_3O_8	166*	167	163	161

* $= \Delta S_{298}$

$\underline{UO_3}$. Kirshenbaum (SAM Columbia 1) gave the following equations for the standard free energy of formation of UO_3 from UO_2 or U_3O_8 and oxygen:

(28) $UO_2 + \frac{1}{2}O_2 \longrightarrow UO_3$:

$$-\Delta F^\circ = 33.830 - 9.32\ T + 0.401 \times 10^{-3}\ T^2 + 1.16 \times 10^5\ T^{-1} - 1.37\ T \ln T$$

(29) $U_3O_8 + \frac{1}{2}O_2 \longrightarrow 3UO_3$:

$$-\Delta F^\circ = 24,600 + 35.1\, T - 1.38 \times 10^{-3}\, T^2 + 0.32 \times 10^{-6}\, T^3 + 4.10 \times 10^5\, T^{-1} - 7.33\, T \ln T$$

leading to values tabulated in Table 32.

TABLE 32

FREE ENERGY OF OXIDATION OF UO_2 AND U_3O_8 TO UO_3

T°K	300	400	500	600	1000
$-\Delta F^\circ$ for reaction (28) kcal/mole UO_2	29.1	27.2	25.2	23.3	15.6
$-\Delta F^\circ$ for reaction (29) kcal/mole U_3O_8	22.6	21.0	19.1	17.2	8.0

MacWood and Altman (UCRL 2) used 288 kcal/mole for the $-\Delta H$ of UO_3 formation from the elements at 298°K, a value which they obtained by substituting a corrected value for the heat of formation of UCl_4 into the calculations of Biltz and Fendius (cf. Table 28). They further estimated $S^\circ_{298} = 22$ E.U. (cf. p.   ) and, using the specific heat equations for uranium and UO_3, derived the following equations for the heat and free energy of formation of UO_3:

(30) $$\Delta H = -289,400 + 6.39\, T - 5.04 \times 10^{-3}\, T^2 - 1.29 \times 10^4\, T^{-1} \text{ cal/mole}$$

(31) $$\Delta F^\circ = -289,400 - 14.72\, T \log T + 5.04 \times 10^{-3}\, T^2 - 6.5 \times 10^3\, T^{-1} + 68.2\, T$$

These equations give:

$\Delta H_{298} = -288$ kcal/mole

$\Delta F^\circ_{298} = -269.1$ kcal/mole

$\Delta S_{298} = -63.6$ E.U.

Brewer (MP Berkeley 1) calculated the following values of the function $(\Delta F_T - \Delta H_{298})/T$ for the formation of UO_3 from the elements:

TABLE 33

ENTROPY OF FORMATION OF UO_3 AT VARIOUS TEMPERATURES

T°K	298	500	1000
$(F_T - H_{298})/T$ cal/(°K mole UO_3)	62.0*	61.7	60.6

* = S_{298}

Fierlé (1919) prepared pastes from gelatine and finely powdered uranium oxides (or hydroxides) and measured the potential of platinum electrodes covered by these pastes and immersed in uranyl nitrate solution (14.3 g $UO_2(NO_3)_2/\ell$) against a normal calomel electrode. He obtained the following values the meaning of which is not clear:

TABLE 34

POTENTIAL OF PLATINUM ELECTRODES WITH URANIUM OXIDES

UO_2 or U_3O_8	$UO_3 \cdot H_2O^+$	$U_3O_{10} \cdot 2H_2O^*$
-0.773 to -0.787 v	-0.860 v	-0.687 v

+ Yellow hydroxide obtained by electrolysis of uranyl acetate.

* Black hydroxide obtained by electrolysis, see p. 118.

Free energies of reduction of UO_3 and U_3O_8 by hydrogen are given in Section 4.4(e) of this chapter (p. 84).

4.2 Reduction of Uranium Oxides to Metal

The reduction of uranium oxides to metal is treated in Chapter IV. Because of the high stability of UO_2 (p. 72) reduction to the metal can be achieved only by very strong reductants, such as the alkaline earth metals.

4.3 Formation of UO by Oxidation of Uranium Metal or Reduction of UO_2

Uranium metal exposed to air at room temperature becomes covered by brownish-black uranium dioxide; green-black U_3O_8 is formed on heating. (Cf. Chapter 6) However, if the oxygen pressure is very low (10^{-9} atm) and the temperature is above 800°C, a grey film is formed which contains a more or less large fraction of uranium monoxide recognizable by its characteristic x-ray diffraction pattern (MP Ames 8). The amount of UO (relative to that of UO_2) increases upon prolonged heating. After five hours of "vacuum" annealing at 800°C, the x-ray pattern of the oxide film showed almost no UO_2 lines (British 1,3).

A mixture of UO_2 and uranium metal powder can be converted into UO:

(32) $$UO_2 + U \longrightarrow 2UO$$

However, this reaction is so slow, even at 2000°C, that equilibrium could not be reached so far even in prolonged experiments (MP Ames 9). In the most successful preparation to date (MP Ames 9,10) heating of a (UO + U) powder mixture to 1900°C gave a product containing 90.6 per cent uranium and 0.24 per cent carbon. Assuming the rest to be oxygen, this preparation must have been approximately one-third UO and two-thirds UO_2.

At Battelle (Battelle 1) the cubic phase with a lattice constant of 4.93 A was observed in the study of uranium-molybdenum alloys and interpreted as UO, formed by oxidation of the metal powder by the residual gas present during the heat treatment in evacuated quartz tubes.

Remarkably, the UO phase appeared much stronger in samples evacuated by means of a mercury diffusion pump than in those evacuated by a mechanical pump.

The straight thermal decomposition of UO_2 into UO and uranium, which occurs only at very high temperatures, has not yet been studied in detail. According to Greenwood (1908) uranium dioxide first begins to lose oxygen in vacuum at about 1600°C.

4.4 Formation of UO_2 from Uranium or Higher Uranium Oxides

(a) Oxidation of Uranium Metal to UO_2. Oxidation of uranium metal by air at room temperatures leads to the formation of brown dioxide, UO_2; prolonged exposure or heating gives green-black U_3O_8. On massive metal the first oxide layer formed tends to protect the rest from oxidation (MP Ames 5). (For more details of uranium behavior in air, see Chapter 6.)

Since the free energy of formation of UO_2 (-122 kcal/g atom oxygen) is much more negative than that of water (-57 kcal/g atom oxygen), uranium is thermodynamically capable of reducing water with the formation of UO_2. Massive uranium reacts with cold water only very slowly (Péligot, 1842a) (Lely and Hamburger, 1914); uranium powder reacts slowly at room temperature and more rapidly at 100°C (Moissan, 1893,1896). Very finely divided uranium (obtained by the decomposition of UH_3) decomposes water rapidly even in the cold.

According to Columbia observers (SAM Columbia 4) UO_2 obtained by treating uranium metal with water is pyrophoric, i.e., it oxidizes spontaneously to U_3O_8 in air.

(b) Thermal Decomposition of U_3O_8 or UO_3 to UO_2 and O_2. According to p. 75 the standard free energy of decomposition of U_3O_8 at room temperature into UO_2 and O_2 is about 21.5 kcal/g atom uranium (21.7 kcal after MacWood and Altman, 21.2 kcal after Kirshenbaum); the free energy of decomposition of UO_3 into UO_2 and O_2 is 29.1 kcal/g atom uranium. One could thus expect both U_3O_8 and UO_3 to be easily convertible to UO_2 by heating in vacuum. However, the above given values represent the average or integral free energies of decomposition; the true or differential free energy of decomposition increases far above this average in the solid solution range below $UO_{2.30}$ (cf. the decomposition isothermals in Fig. 6). Experiments by Biltz and Müller (1927) described in more detail in section 1 (p. 13) indicate that because of this the decomposition of U_3O_8 usually stops (in the normally obtainable vacua and at temperatures up to 1300°C) at an approximate composition of $UO_{2.15}$.

In air the decomposition of U_3O_8 begins at about 900°C, the temperature at which the decomposition pressure of stoichiometrically pure $UO_{2.667}$ reaches the partial pressure of oxygen in the air (Colani, 1907) (Biltz and Muller, 1927). Since between $UO_{2.667}$ and $UO_{2.61}$ the decomposition pressure drops rapidly with decreasing oxygen content, the decomposition of U_3O_8 stops after only very little oxygen has been lost, unless the oxygen pressure over the oxide has been reduced far below that in the open air or the temperature raised considerably above 1000°C. According to Fig. 2 in the constant pressure range, $UO_{2.62}$ to $UO_{2.30}$, the decomposition pressure of oxygen is only 0.3 mm at 1160°C; by the time the composition $UO_{2.20}$ has been reached this pressure has dropped to 0.02 mm.

The isothermals reproduced in Fig. 2 show how far the decomposition can be expected to progress, according to Biltz and Müller, under various oxygen pressures at temperatures up to 1160°C.

The thermal decomposition of U_3O_8 also was studied by TEC investigators (CEW-TEC 3). They started with $UO_{3.0}$, $UO_{2.64}$ and $UO_{2.61}$ as material and found that in evacuated sealed tubes no decomposition beyond the formula $UO_{2.61}$ took place at 700°C. The oxygen pressure increase after ignition was 34 mm with UO_3, and 2.4 mm with $UO_{2.64}$; no oxygen was evolved at all with $UO_{2.61}$. At 750°C-830°C after twelve hours heating of UO_3 in high vacuum, the residue still had the composition $UO_{2.55}$ and $UO_{2.62}$. These results confirm the conclusion drawn above from the observations of Biltz and Müller, that the thermal decomposition of U_3O_8 at temperatures below 1000°C stops considerably short of the composition $UO_{2.5}$ even in high vacuum.

According to Jolibois and Bossuet (1922) complete decomposition of U_3O_8 to UO_2 and oxygen can be obtained by heating to 2000°C in vacuum.

It has been asserted that U_3O_8 can be completely de-oxygenated also in a stream of oxygen-free indifferent gas instead of high vacuum. For example, Zimmermann, Alibegoff and Krüss (1886a) claimed to have obtained pure brown UO_2 by igniting U_3O_8 over the gas flame in a platinum crucible in nitrogen or carbon dioxide, and Friederich and Sittig (1925) described the formation of brown UO_2 by heating UO_3 in hydrogen stream to about 1000°C, and of a dark "blue" dioxide (cf. p. 34) by heating UO_3 in a stream of nitrogen to 1100°C. The assertion that the latter product also had the exact composition $UO_{2.00}$ appears somewhat doubtful in the light of our present knowledge about the difficulty of complete conversion of U_3O_8 to UO_2.

The de-oxygenation of UO_3 will be described in more detail in section 4.5 when dealing with the conversion of this oxide to U_3O_8. Some observations indicate, however, that UO_3 may be converted to UO_2 without the intermediate formation of the U_3O_8 phase (cf. below, p. 90).

(c) Reduction of UO_3 and U_3O_8 to UO_2.

Reduction of UO_3 or U_3O_8 by Hydrogen to UO_2. While uranium metal can liberate hydrogen from water forming UO_2, hydrogen is able to reduce the higher uranium oxides, UO_3 and U_3O_8, to UO_2; the free energy of reduction (with formation of H_2O gas) is, according to the estimates made by Columbia University (SAM Columbia 12), given by equations (33) and (34):

(33) $UO_3 + H_2 \longrightarrow UO_2 + H_2O$ (g);

$$-\Delta F^{\circ} = 22{,}890 + 16.42\ T - 0.79 \times 10^{-3}\ T^2 + 0.22 \times 10^{-6}\ T^3 - 0.69 \times 10^5\ T^{-1} - 1.17\ T \ln T \quad \text{cal/mole}$$

(34) $U_3O_8 + 2H_2 \longrightarrow 3UO_2 + 2H_2O$ (g);

$$-\Delta F^{\circ} = 36{,}545 + 77.3\ T - 3.36 \times 10^{-3}\ T^2 + 0.762 \times 10^{-6}\ T^3 + 1.96 \times 10^5\ T^{-1} + 11.32\ T \ln T \quad \text{cal/mole}$$

The evaluation of ΔF from these equations gives values tabulated in Table 35.

TABLE 35

FREE ENERGY OF REDUCTION OF UO_3 AND U_3O_8 TO UO_2 BY HYDROGEN

Reaction	$-\Delta F$				
	300°K	400°K	500°K	600°K	1000°K
(33) kcal/mole UO_3	25.5	26.4	27.2	27.9	30.6
(34) kcal/mole U_3O_8	45.8	47.5	49.0	50.3	54.0

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Related to one g atom uranium, the free energy of reduction to UO_2 by hydrogen at room temperature is 25.5 kcal for UO_3 and 15.3 kcal for U_3O_8.

The above given free energy values were based on Burton and Davis' (MP Chicago 9) calculation of the free energy of reaction (34) and were used at Columbia also for the calculation of the free energy of formation of U_3O_8 (cf. equation (24) on p. 76). One could, of course, also reverse the procedure and use the free energy of formation of U_3O_8 (as estimated by MacWood and Altman, cf. equation (27)) for the calculation of the free energy of reduction of U_3O_8 by hydrogen.

Preparation of UO_2 by reduction of the higher oxides with hydrogen was first described by Arfvedson (1822a,1824), Lecanu (1825), Laugier and Boudet (1825) and later by Sabatier and Senderens (1895). The same method was used by Aloy (1900), Oechsner de Coninck (1908), Jolibois and Bossuet (1922), Lebeau (1922), Goldschmidt and Thomassen (1923b), and Biltz and Müller (1927). Some disagreement exists as to the temperature required for complete reduction to $UO_{2.00}$, particularly in the case of U_3O_8 as starting material. Lebeau (1922) found that U_3O_8 is rapidly and completely reduced by hydrogen to brown $UO_{2.0}$ at 900°C-1000°C without the formation of intermediary oxides. Biltz and Müller (1927) also have prepared stoichiometrically pure dioxide by reduction of U_3O_8 by H_2 at 900°C-1000°C; they obtained in this way a brown dioxide from green U_3O_8 and a darker, purplish-brown dioxide from black, strongly ignited U_3O_8 (both products analyzed as $UO_{2.0}$). Jolibois and Bossuet (1922) asserted that a temperature of 625°C-650°C is sufficient for complete reduction of U_3O_8 by hydrogen if P_2O_5 is used to remove the water vapor.

British observers (British 4) asserted, on the other hand, that the reduction of U_3O_8 by hydrogen at 650°C-680°C stops at $UO_{2.14}$ ($=UO_3 \cdot 6UO_2$), the same composition which is obtained by decomposition of U_3O_8 in vacuum at temperatures up to 1300°C. They suggested that the reduction of U_3O_8 by hydrogen consists of two stages, thermal decomposition of the oxide and reduction of liberated oxygen with hydrogen; therefore, the whole reaction stops when the decomposition pressure of the oxide becomes negligible, which, according to p. 82 , occurs when the oxygen content is reduced to about $UO_{2.15}$.

It seems, however, unlikely that hydrogen should not react directly with the solid oxide. Even if it proves true that (at 680°C) the reduction of U_3O_8 with hydrogen stops at $UO_{2.15}$, one will be inclined to attribute this to a high <u>activation energy</u> of the direct reaction of $UO_{2.15}$ with hydrogen, while the thermal decomposition of U_3O_8 stops at the same composition because of the high <u>energy of reaction</u> even at temperatures as high as 1300°C. The statement of the British authors that, according to Newberry and Pring (1916), a temperature of 2000°C and a hydrogen pressure of 150 atm are required for complete reduction of $UO_{2.15}$ to $UO_{2.00}$ disregards the observations of Lebeau and of Biltz and Müller, who obtained stoichiometrically pure $UO_{2.0}$ by U_3O_8 reduction with hydrogen at 900°C under only one atm of hydrogen (cf. above).

According to the Tennessee Eastman Company observers (CEW-TEC 1) the ease with which U_3O_8 can be reduced by hydrogen depends on the history of the sample. In a first investigation two hours sintering at 700°C-730°C gave an oxide with $\rho = 3.2-3.6$ which could be reduced at 500°C-700°C; while at $\rho > 3.5$, complete reduction became difficult. In a more detailed study (CEW-TEC 4) the data in Table 36 were obtained.

TABLE 36

RATE OR REDUCTION OF U_3O_8 by H_2

Preparation	Rate of Reduction at 550°C (mole H_2 per mole uranium per min)
U_3O_8 prepared from oxalate at 350°C	0.036
U_3O_8 prepared from ammonium diuranate at 800°C	0.029
U_3O_8 prepared from peroxide at 800°C	0.026
U_3O_8 calcined at 600°C, bulk density 1.60	0.046
" " " 700°C, " " 2.24	0.032
" " " 805°C, " " 2.33	0.029
" " " 900°C, " " 2.54	0.019

These experiments show clearly the effect of surface area (which is reduced by sintering at higher temperatures). Certain impurities exercise a strong influence on the rate of reduction of U_3O_8 by hydrogen:

Pure U_3O_8	0.057	mole H_2/(mole uranium x min)
U_3O_8 + 1% Fe_2O_3	0.059	"
U_3O_8 + 3% SiO_2	0.023	"
U_3O_8 + 1% Al_2O_5	0.007	"

This effect, too, is typical of a surface reaction.

In a further study of the kinetics of UO_3 and U_3O_8 reduction by hydrogen at the TEC (CEW-TEC 2) UO_3 was used as the semihydrate, $UO_3 \cdot \frac{1}{2}H_2O$, prepared from uranyl nitrate by precipitation and heating to 250°C-300°C for two and one-half hours; U_3O_8 was prepared by calcination of UO_3 at 800°C.

The reduction of UO_3 in a closed tube at temperatures above 500°C was found to cause an initial increase in pressure while no such increase was observed with U_3O_8. It therefore appears that the first stage in the reduction of UO_3 in fact is thermal decomposition into U_3O_8 (or a slightly lower oxide) and oxygen, but that U_3O_8 is reduced directly by hydrogen. If finely dispersed copper is present during the decomposition of UO_3, thus catalyzing the $H_2 + O_2$ combination, no increase in pressure is observed.

The effect of hydrogen pressure on the rate of reduction of U_3O_8 at 520°C is shown in Fig. 11. The curves show a "saturation" effect typical of surface reactions whose rate is determined by adsorption. The small difference between initial and final rate also is characteristic of this type of reactions. Fig. 12 shows the effect of temperature on the initial rate of reduction under 400 mm hydrogen pressure. Below about 550°C the reaction has an activation energy of about 30.7 kcal/mole; above this temperature it becomes almost independent of temperature and even decreases slightly above 700°C.

The high activation energy cannot correspond to the rate of adsorption of hydrogen by the oxide since activated hydrogen adsorption by various oxides has an activation energy of only 10-20 kcal/mole. The authors therefore assume that equilibrium between adsorbed and free hydrogen is not disturbed by reduction. The rate is then proportional to the equilibrium concentration of adsorbed hydrogen and determined by the activation energy of some slow reaction step, perhaps the transformation of the tetragonal U_3O_8 lattice into the cubic UO_2 lattice (which occurs discontinuously when $UO_{2.61}$ (according to Biltz) or $UO_{2.55}$

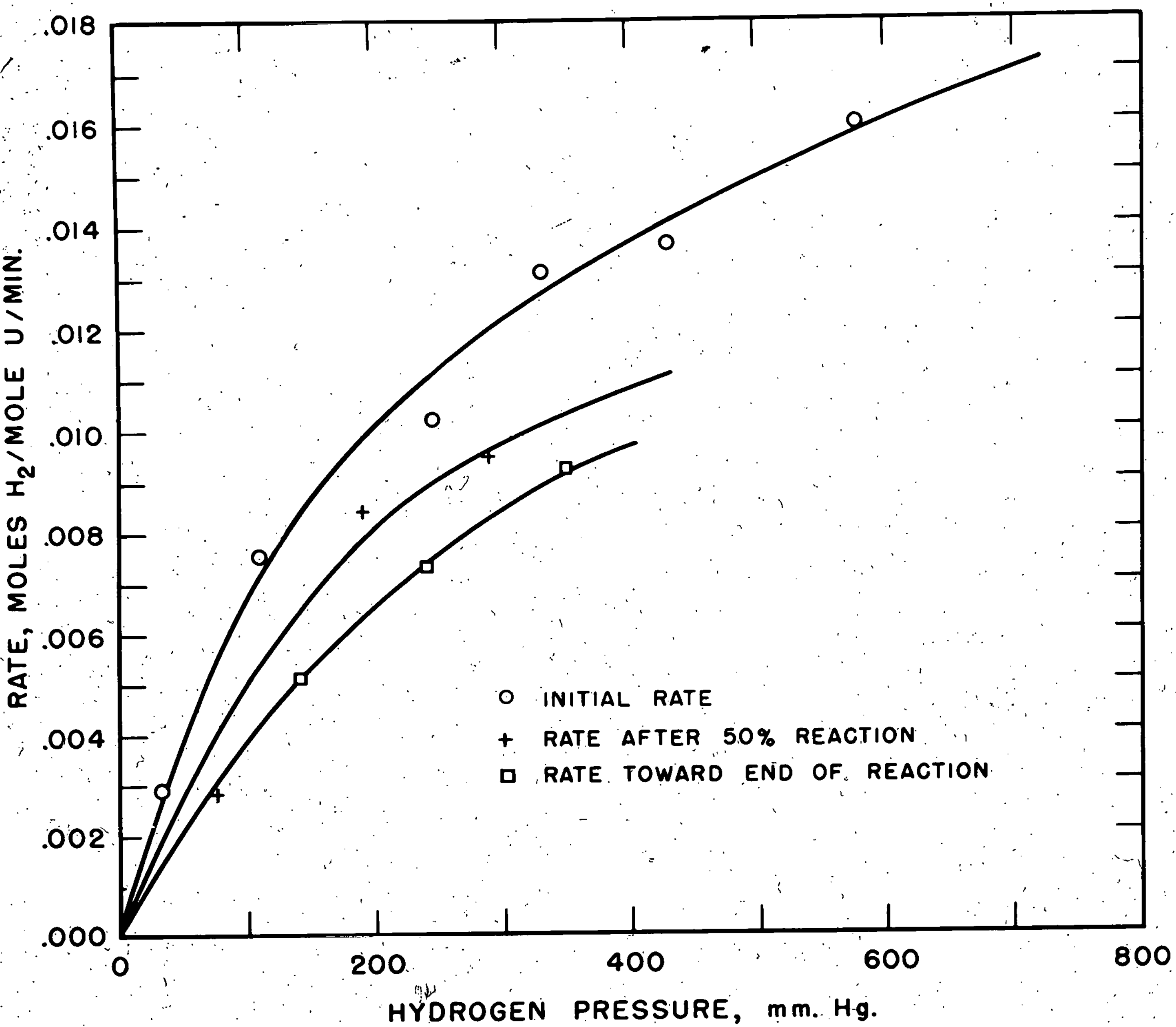

FIG. 11. EFFECT OF HYDROGEN PRESSURE ON U_3O_8 REDUCTION.

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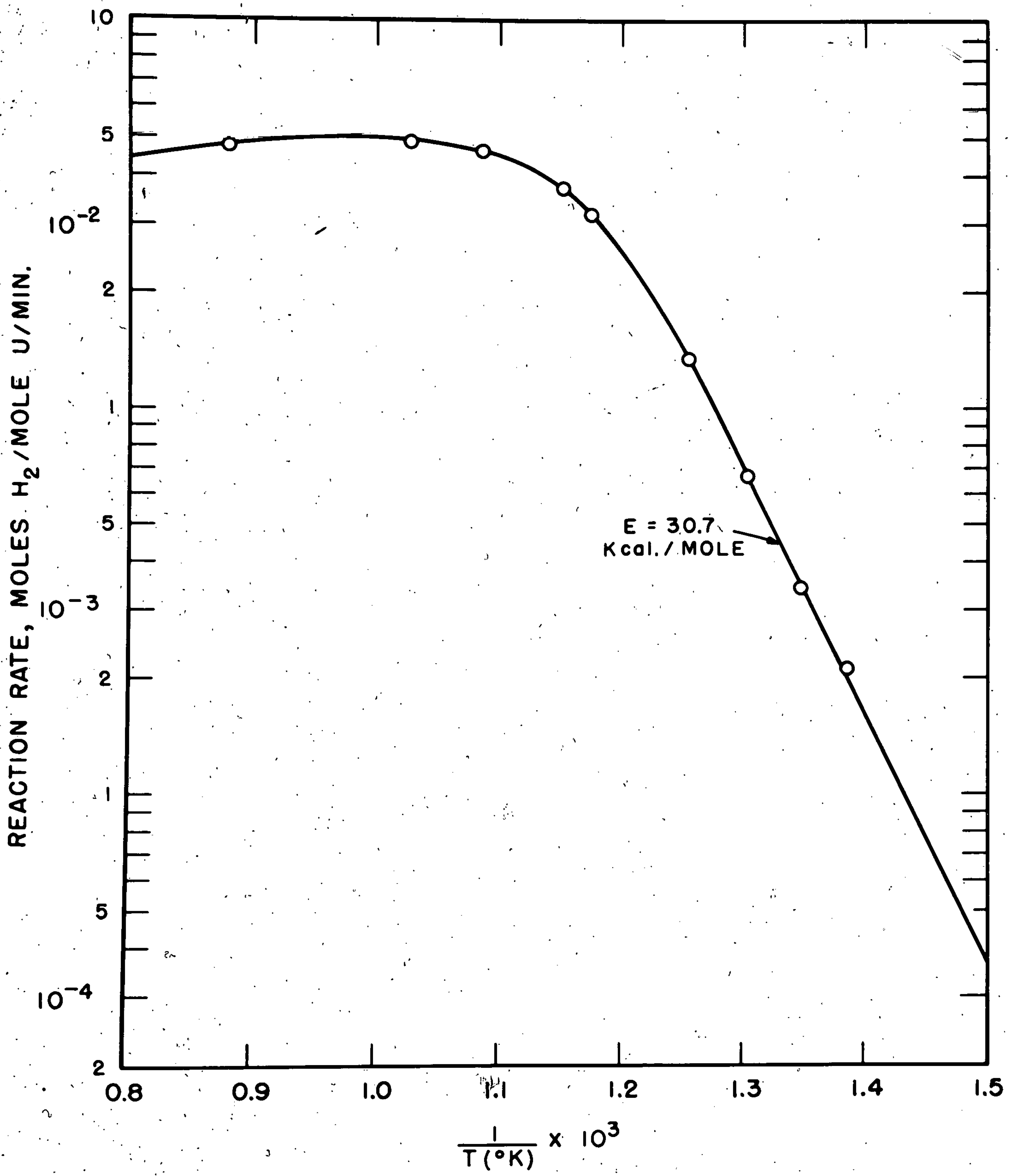

FIG. 12. ACTIVATION ENERGY OF U_3O_8 REDUCTION

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(according to the TEC authors) is transformed into $UO_{2.30}$. The optimum temperature of reduction corresponds to a maximum of the function $V = V_{ads}\ e^{-E_A/RT}$, where the adsorbed volume V_{ads} decreases with temperature while the exponential function, containing the activation energy E_A, increases with temperature.

The decrease in rate with the progress of reaction is more rapid than can be explained by the decreasing adsorption area and suggests a slight increase in activation energy towards the end of the reaction.

Experiments (Table 37) with three U_3O_8 samples with different surface areas confirmed the parallelism between rate and surface development already demonstrated in Table 36.

TABLE 37

RATE OF REDUCTION OF U_3O_8 BY HYDROGEN

Source	Calcination T°C	Surface	Rate $\left(\frac{\text{moles } H_2}{\text{mole U x min}}\right)$	
			at 380°C	at 545°C
UO_4	850	small	0.0002	0.019
$(NH_4)_2U_2O_7$	650	medium	0.0010	0.057
$UO_2C_2O_4$	350	great	0.0023	0.036*

* Probably area reduced by sintering

The reduction of U_3O_8 by hydrogen under water at low temperatures and under high pressure of hydrogen was studied at Columbia University (SAM Columbia 13). For this purpose the oxide slurries were heated in steel bombs with pyrex lining. Under a hydrogen pressure of 120 psi at 175°C-310°C the reduction was very slow (20 per cent reduction after one hundred and fifty hours). The effects of temperature and pressure on the rate of reduction are illustrated by the following two tables:

TABLE 38

REDUCTION OF U_3O_8 BY HYDROGEN

A. EFFECT OF TEMPERATURE AT 140 PSI

t°C	per cent reduction in two hours
150	1
200	3.5
250	6
300	9

B. EFFECT OF PRESSURE AT 250°C

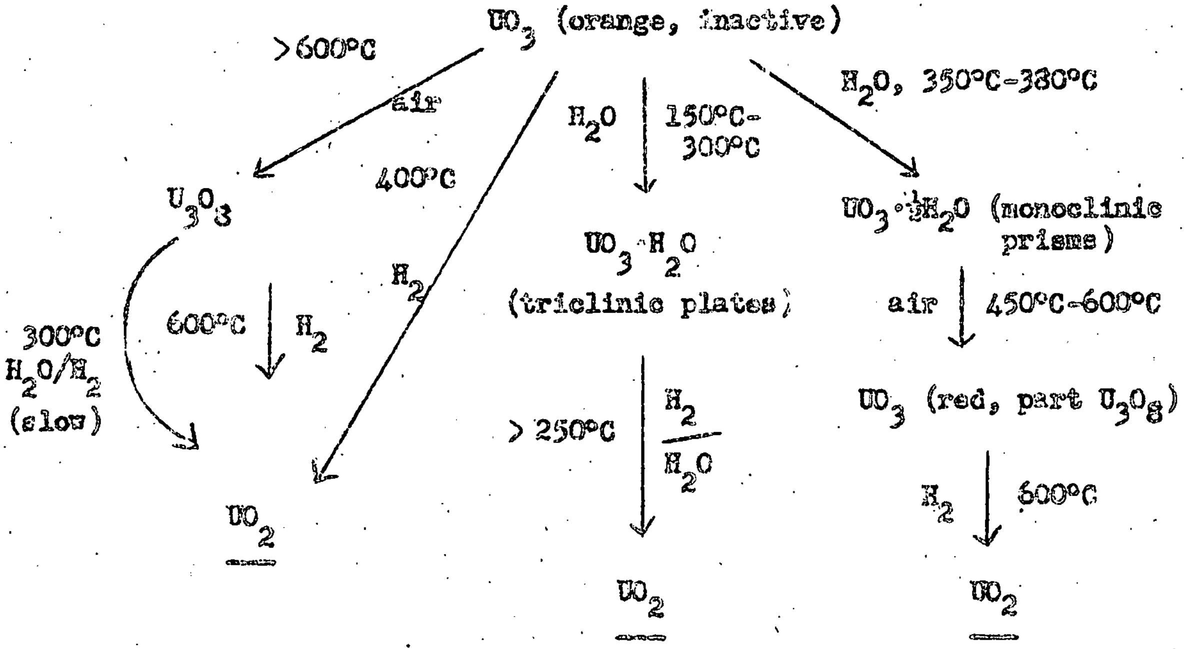
psi	per cent reduction in two hours
70	3
95	4.8
140	5.5

According to the previously mentioned British paper (British 4) brown, stoichiometrically pure $UO_{2.0}$ can be obtained by reduction with hydrogen at temperatures as low as 650°C if UO_3 is used as initial material instead of U_3O_8. This seems to indicate that the reduction of UO_3 to UO_2 proceeds without the intermediate formation of U_3O_8 (which is not too easy to understand since, according to p. 43 , the UO_3(I) lattice is converted into the U_3O_8 lattice by a gradual loss of oxygen without formation of a new phase).

That UO_3 can in fact be reduced to $UO_{2.0}$ by hydrogen at low temperatures (compared to those required for the reduction of U_3O_8) has been confirmed by many observers. At Columbia University (SAM Columbia 2) uranium dioxide was prepared by reduction of UO_3 by oxygen-free hydrogen at 650°C; at Brown University (Brown 4) it was found that heating to 400°C-550°C is sufficient to start the reaction which then liberates sufficient heat to make the mass glow. At the Mallinckrodt Chemical Company (Mallinckrodt 1) a factory process is in use in which orange UO_3 is reduced to brown UO_2 in a stream of hydrogen at 815°C (1500°F); it is stated, moreover, that reduction can be achieved even at much lower temperatures. Linde Air Products (Linde 1) carried out the same reduction at 700°C; they state that the results at 670°C or lower are unsatisfactory. The amount of excess hydrogen used was found to markedly affect the subsequent reactivity of the product.

The exact temperature required for the reduction of UO_3 to UO_2 by hydrogen depends on the form of the trioxide. For example, at Columbia University (SAM Columbia 4) the orange-red trioxide obtained by heating $UO_4 \cdot 2H_2O$ to 250°C was found to be "active"; it could be reduced by hydrogen above 300°C and gave "active" (pyrophoric) UO_2. On the other hand, the orange-yellow UO_3 obtained by ignition of uranyl nitrate at 700°C in oxygen was comparatively unreactive and was only reduced by hydrogen at 400°C. According to p. 42 , the explanation of these differences must be sought in the fact that the first method of preparation of the trioxide leads to amorphous UO_3 while the second one gives the more stable crystalline UO_3(III).

The following scheme reviews different paths by which "inactive" UO_3 was converted to UO_2 at the Columbia laboratories:



Reduction of UO_3(II) to UO_2

A UO_3 slurry was found to be stable in hydrogen below 265°C; at 310°C it was 3 per cent reduced in twenty-four hours.

At Columbia University (SAM Columbia 13) the reduction of the hydrate $UO_3 \cdot H_2O$ by hydrogen was further studied in steel bombs with pyrex liners. The reduction was very slow, e.g. at 310°C, only 3.7 per cent was reduced after one hundred and fifty hours under 120 psi. No difference in the rate of reduction was noted between rhombic and triclinic modifications of $UO_3 \cdot H_2O$.

In another experiment with $UO_4 \cdot 2H_2O$ as starting material the peroxide was found completely decomposed to UO_3 after forty-eight hours at 310°C but no reduction of the latter took place at all. One difference between this and the $UO_3 \cdot H_2O$ experiments which might have affected the results was the presence of platinum and copper surfaces in the apparatus in the experiment with the peroxide.

In the reduction of U_3O_8 or UO_3 by hydrogen there is apparently no danger of reaction proceeding beyond the composition $UO_{2.0}$. As mentioned on p. 72 , UO_2 is thermodynamically stable in hydrogen as far as conversion to uranium (and probably also to UO) is concerned. One is less certain whether a reduction to UO_x $(1 < x < 2)$ may not be thermodynamically possible (cf. p.), but experiments gave no indications of any reduction of UO_2 by hydrogen even under such extreme conditions as p = 25 atm, t = melting point of tungsten (v. Wartenberg, Broy and Reinicke, 1923); p = 150 atm, t = 2500°C (Newbury and Pring, 1916a); and p = 100 atm, t = 1100°C (Rideal, 1914). Faehr (1908) observed no reduction of UO_2 in a high voltage arc in hydrogen. Columbia University investigators (SAM Columbia 4) noted that UO_2 slurries in water were stable in hydrogen up to 250°C.

Reduction of U_3O_8 or UO_3 by Metals and Metal Oxides. According to Gay-Lussac and Thénard (1811) U_3O_8 is reduced to UO_2 by potassium at about 150°C with weak evolution of heat. At the Mallinckrodt Chemical Company (Mallinckrodt 2) a method of reduction of UO_3 by means of magnesium was developed on plant scale. Magnesium reduces orange UO_3 to brown UO_2

at 500°C; no reduction of UO_2 by Mg occurs under these conditions. Tammann and Rosenthal (1926) observed the reduction of UO_3 by ferrous oxide and stannous oxide in the heat.

Reduction of U_3O_8 or UO_3 by Carbon. Uranium dioxide was first prepared by Klaproth (1789) by reducing U_3O_8 with carbon. Because of the black color of the powder and its metallic lustre, he took it to be the metal; the error was recognized only fifty years later by Péligot (1842a,b). According to Moissan (1892) reduction of U_3O_8 to uranium by carbon is possible only in an electric furnace at 3000°C.

According to Aloy (1901) UO_2 is formed in the electric furnace from U_3O_8 (or UO_3) and carbon if the temperature is not high enough for the formation of uranium carbide.

Reduction of U_3O_8 and UO_3 by Methane. At Berkeley (UCRL 3,4) it was found that the conversion of bright-red UO_3 to UO_2, which is slow at 500°C in air, nitrogen or oxygen, is accelerated and leads rapidly to black UO_2 if CH_4 is introduced. The reaction begins at 400°C. At 450°C the product was a mixture of UO_2 and U_3O_8.

Reduction of U_3O_8 or UO_3 by Sulfur, Hydrogen Sulfide or Carbon Disulfide. Hermann (1861) obtained UO_2 by igniting U_3O_8 (or sodium uranate) with sulfur and ammonium chloride and washing the product with water, as well as by ignition of UO_3 or U_3O_8 in dry carbon dioxide saturated with carbon disulfide vapor. However, this reaction is now known to be complex and may produce oxysulfides instead of the dioxide. Kohlschütter (1901) found that UO_3 is reduced to UO_2 by hydrogen sulfide in alkaline, neutral, or even weakly acid solution.

Reduction of U_3O_8 with Ammonia or Ammonium Chloride. Smith and Matthews (1895) obtained a reddish-brown uranium oxide containing no nitrogen or chlorine by heating U_3O_8 to white heat for six hours with a large excess of ammonium chloride. The porcelain crucible containing the mixture was placed in a larger unglazed crucible and surrounded with charcoal to provide a reducing atmosphere.

The reduction of UO_3 or U_3O_8 with ammonia was studied at the Tennessee Eastman Company (CEW-TEC 5) and found to represent a convenient method for the conversion of U(VI) to U(IV) compounds.

Almost no reduction of UO_3 by ammonia was found to take place below 250°C (except for occasional formation of a green surface layer). At 250°C-400°C the reduction appears to proceed only to the composition U_3O_8 (even this represents, however, a stronger reduction than could be achieved at these temperatures by straight thermal decomposition). Above 450°C reduction to UO_2 sets in and becomes complete (more complete than with hydrogen as reductant) at 550°C.

Reduction of U_3O_8 with Oxalic Acid. Wertheim (1843) obtained black, easily oxidizable UO_2 by heating U_3O_8 with oxalic acid in the absence of air. Oechsner de Coninck and Raynaud (1911) reduced U_3O_8 to UO_2 by calcium oxalate at red heat.

Reduction by Ethanol Vapor. U_3O_8 can be reduced to UO_2 by ethanol vapor at or above 200°C.*

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* Referred to in CEW-TEC 3.

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4.5 Conversion of UO_2 and UO_3 to U_3O_8

(a) Oxidation of UO_2 to U_3O_8. Oxidation of UO_2 by Oxygen. Thermodynamically, U_3O_8 is stable only in a rather narrow range of temperature, e.g. at p_{O_2} = 10 mm between 580°C and about 750°C (cf. Fig. 4) or in air ($p_{O_2} \simeq$ 150 mm) between about 650°C and 900°C (Colani, 1907), (Biltz and Müller, 1927). Practically, however, U_3O_8 is obtained in a stoichiometrically more or less pure state by ignition of both lower and higher uranium oxides in air. (The usual method of gravimetric determination of uranium as U_3O_8 is based on this fact.) This practical stability of U_3O_8 is due to the difference between the rates of oxidation of the lower uranium oxides to U_3O_8 and of U_3O_8 to UO_3. The first process occurs easily even at rather low temperatures while the second one is very slow: according to p. 18 U_3O_8 is not oxidized to UO_3 in air at low temperatures except perhaps in geological times. At elevated temperatures (of the order of 350°C) U_3O_8 can be oxidized in the laboratory only if it is present in an especially active, finely dispersed form. To oxidize ordinary U_3O_8 rapidly to UO_3 one has to use oxygen pressures of the order of 100 psi.

Because of this difference in the rate of oxygen uptake below and above the composition $UO_{2.67}$, ignition of lower oxides in air leads to the formation of practically pure U_3O_8 even if the temperature of heating is one at which UO_3 is the thermodynamically stable oxide (< 650°C). If the decomposition temperature of U_3O_8 (about 900°C in air) has been exceeded in the process of ignition, the missing oxygen is likely to be recovered during cooling (unless the latter is very rapid, cf. Zimmermann, Alibegoff and Krüss, 1886) but no oxygen in excess of the formula $UO_{2.67}$ will be taken up.

The temperature to which UO_2 has to be brought in air for oxidation to U_3O_8 depends on the "activity" of the sample, i.e., probably on its degree of dispersion. According to Jolibois and Bossuet (1922) rapid oxidation of ordinary UO_2 begins at about 185°C. "Pyrophoric" UO_2 samples, which oxidized in air at room temperature with incandescence, have been prepared by Péligot (1842) by decomposition of oxalate. According to Columbia University observers (SAM Columbia 4) similarly unstable uranium dioxide is obtained by reaction of uranium metal with boiling water. At the UCRL (UCRL 6) it was found that UO_2 obtained by reduction of UO_3 with natural gas also is pyrophoric, and the same observation was made in Britain (British 4) with brown UO_2 obtained by reducing UO_3 by hydrogen at 650°C.

Oxidation of UO_2 to U_3O_8 by Oxidants Other than Oxygen. The free energy of formation of U_3O_8 from UO_2 and oxygen (ΔF° = -64 kcal/mole U_3O_8 at 300°K and -38 kcal/mole at 1000°K, cf. p. 76) is considerably less negative than the free energy of formation of an equivalent quantity of water (ΔF° = -109 kcal for two moles H_2O at 300°K and -92 kcal for two moles H_2O at 1000°K); therefore, UO_2 cannot be expected to reduce water. Regnault (1856) thought that steam oxidizes UO_2 to U_3O_8 but Chaudron (1921) was unable to confirm this observation. Columbia University observers (SAM Columbia 4) found no effect of water vapor on UO_2 at 310°C. Sabatier and Senderens (1892,1895,1896) studied the oxidation of UO_2 by nitrogen oxides. N_2O did not attack brown UO_2 (prepared by UO_3 reduction with hydrogen at red heat) but reacted slowly with black UO_2 prepared at lower temperatures. NO reacted with brown UO_2 below red heat with heat evolution and formation of a black product which the authors considered to be U_2O_5. NO_2 reacted with both brown and black UO_2 in the cold with strong evolution of heat.

(b) Decomposition of UO_3 to U_3O_8. Thermal Decomposition. As described in section 4.5 (a), U_3O_8 can be obtained by thermal decomposition of UO_3. The isothermals (cf. Fig. 2) indicate that in oxygen at one atmosphere pressure decomposition of UO_3 should begin a little below 470°C and the decomposition to U_3O_8 should be reached somewhere above 650°C. With free access to air ($p_{O_2} \simeq 150$ mm) complete decomposition to U_3O_8 should occur at about 650°C. In vacuo decomposition should be complete below 580°C. It was mentioned on p. 17 that in practice the decomposition of UO_3 may be delayed indefinitely or begin only after an induction period of one or several days. Sometimes it occurs only when the decomposition temperature has been considerably exceeded (or when the pressure was made much lower than the equilibrium decomposition pressure).

These complications are due to the existence of at least four (and perhaps as many as six) allotropic modifications of UO_3 of different stability. According to Fried and Davidson (MP Chicago 3) the results of Biltz and Müller were obtained at the lower temperatures with amorphous UO_3 formed by thermal decomposition of UO_4·aq. At the higher temperatures they probably dealt with the hexagonal form UO_3(I). Oechsner de Coninck noticed in 1901, 1904a that the brick-red form of UO_3 obtained by prolonged heating of amorphous trioxide in air is considerably more stable than the initial amorphous orange-red oxide. This brick-red form was probably Fried and Davidson's UO_3(II). According to the last named authors the yellow form UO_3(III), which can be obtained by prolonged heating of UO_3 or U_3O_8 under high oxygen pressure and is also formed by ignition of uranyl nitrate ("Mallinckrodt's oxide"), is still more stable. Under one atm of oxygen UO_3(III) remained unchanged even after one hour at 700°C. This may be due to delayed decomposition but is more likely to represent true thermodynamic stability. Amorphous UO_3 was found by Fried and Davidson to decompose under 1 atm oxygen to $UO_{2.70}$ at 650°C in approximate agreement with the results of Biltz and Müller (1927b). Red UO_3 obtained by Fischer (1913) from uranyl salt solutions by electrolysis and dehydration behaved in a similar way. It began to decompose in air at 470°C and was more or less completely reduced to U_3O_8 at 600°C. Hüttig and Schroeder (1922) noticed the first signs of oxygen liberation from UO_3 in vacuum at 400°C-500°C. Jolibois and Bossuet (1922) observed a rapid dissociation of UO_3 in vacuum at 502°C. Goldschmidt and Thomassen (1923c) noticed U_3O_8 lines in the UO_3 x-ray diffraction pattern after heating to 270°C in air, a result which is difficult to interpret since, according to Zachariasen, UO_3(I) is transformed into U_3O_8 without the formation of a new phase.

Lebeau (1922) must have been dealing with one of the more stable modifications of the trioxide when he observed that UO_3 does not change at all in air up to 600°C. Above 600°C his UO_3 sample was converted into olive green or green-black intermediate oxides and only at 800°C into grey-black U_3O_8. Similarly, Tammann and Rosenthal (1926) observed that UO_3 began to decompose in air only at 670°C with the formation of intermediate green oxides and was completely converted to black U_3O_8 first at 865°C.

v. Schroeder (see Biltz and Müller, 1927) made the peculiar observation that a UO_3 sample which has remained almost unchanged after twelve days at 600°C in air was reduced to $UO_{2.68}$ within twelve hours when a stream of oxygen was passed over it. In this connection one may quote the observation of Fried and Davidson (MP Chicago 3) that brick-red UO_3 (obtained by gas phase oxidation of U_3O_8 by N_2O_4), which was heated for one-half hour to 600°C-650°C under 1 atm oxygen, was found about 87 per cent changed into yellow UO_3(III) (the rest being green U_3O_8).

The formation of oxides intermediate between UO_3 and U_3O_8 by heating to 600°C-650°C was observed also by Fried and Davidson (MP Chicago 3) who obtained $UO_{2.96}$ and $UO_{2.82}$ by heating amorphous UO_3 under 1 atm oxygen for one-half to one hour to 620°C and 650°C respectively. Taylor (1931) noted that at 580°C $UO_{3.04}$ was converted to $UO_{2.91}$ within fifteen minutes but required one hundred and twenty-three hours for conversion to $UO_{2.84}$.

At Columbia University (SAM Columbia 4) it was observed that amorphous anhydrous UO_3 heated to 600°C showed no conversion to U_3O_8; commercial hydrated, yellow UO_3 (7 per cent H_2O, 14 per cent UO_4) lost both water and oxygen at 600°C and was converted to a mixture of UO_3 and U_3O_8.

$UO_3 \cdot \frac{1}{2}H_2O$ lost both oxygen and water above 430°C and was gradually transformed into a mixture of U_3O_8 and UO_3.

The initial rate of de-oxygenation of UO_3 (of unspecified origin) was measured by TEC observers (CEW-TEC 3) with the results shown in Table 39.

TABLE 39

INITIAL RATE OF DECOMPOSITION OF UO_3

t°C	500	590	640	800
$\frac{\text{moles oxygen}}{\text{mole uranium x min}}$	0.007	0.031	0.086	0.192

To sum up, it seems that the "unstable" forms of UO_3, e.g., amorphous trioxide, begin to decompose in air at 400°C-500°C and can be fully converted into U_3O_8 at 650°C while the "stable" forms, e.g., UO_3(III), only begin to decompose in air at 600°C and may have to be heated to 800°C for complete conversion to U_3O_8. It remains to be investigated how far the forms UO_3(II) and UO_3(III) have to be deoxygenated before a transformation into the orthorhombic U_3O_8 phase occurs.

4.6 Formation of UO_3 and its Hydrates from Other Uranium Oxides.

(a) UO_3 Preparation by Oxidation of UO_2 or U_3O_8. UO_3 is the thermodynamically stable uranium oxide in air at temperatures up to about 450°C-600°C (depending on the allotropic form). Between there and about 650°C the stable phases have compositions between UO_3 and $UO_{2.67}$, and only above 650°C does U_3O_8 become the stable uranium oxide in air. Nevertheless, oxidation of UO_2 by oxygen usually leads only to U_3O_8.

In sections 1.4 and 4.5(a) we commented on the slowness of oxidation of U_3O_8 to UO_3 by air or oxygen. Only few cases of direct oxygenation of U_3O_8 to UO_3 have been reported in the literature. Lebeau (1922a) and Bilts and Müller (1927) both observed that finely dispersed, grey-black U_3O_8 obtained by low temperature (350°C) decomposition of uranyl oxalate became orange-brown in air after twelve hours heating to 350°C. Chemical analysis of the product indicated a composition close to UO_3.

At Columbia University (SAM Columbia 13) the oxidation of U_3O_8 by oxygen was studied in water slurries under high oxygen pressure. Stainless steel bombs fitted with pyrex linings were used. Under these conditions oxidation was found to be comparatively rapid; at 100°C-250°C and oxygen pressures of 45-165 psi up to 75 per cent was oxidized in one-half to two hours. Table 40 shows some typical results.

TABLE 40

OXIDATION OF U_3O_8 BY OXYGEN

A. EFFECT OF OXYGEN PRESSURE AT 150°C

Initial Pressure (psi)	per cent U(IV) oxidized to U(VI) in two hours
60	23
90	26
120	31
165	38

B. EFFECT OF TEMPERATURE AT 120 PSI

t°C	per cent U(IV) oxidized to U(VI) in two hours
100	7.5
150	30
200	56
250	76

At the Metallurgical Laboratories (MP Chicago 3,8) U_3O_8 was also converted to UO_3 in the dry state by oxygen under high pressure (30-150 atm). Temperatures of 500°C-750°C were used and UO_3(I)/UO_3(II) or UO_3(III) was obtained depending on the conditions of the experiment (cf. Table 12 on p. 43). The most stable form, UO_3(III), was obtained at the highest temperatures (700°C-750°C) and oxygen pressures (70-150 atm).

At the Tennessee Eastman Company (CEW-TEC 1) U_3O_8 was converted to UO_3 by vapor phase oxidation at 350°C-400°C with nitric acid or, better, with nitrogen tetroxide, N_2O_4 (the latter reagent was prepared by bubbling air or oxygen through HNO_3 at 65°C-80°C).

Oxidation of UO_2 to UO_3 by hydrogen peroxide was studied in some detail at Columbia University (SAM Columbia 4,12). The free energy equation of this process was estimated as follows:

$$(35) \qquad UO_2 + H_2O_2(\text{liq.}) \longrightarrow UO_3 + H_2O(\text{liq.});$$

$$-\Delta F = 58{,}360 - 10.15\,T + 0.465 \times 10^{-3}\,T^2 + 0.69 \times 10^{5}\,T^{-1} + 1.10\,T \ln T$$

Evaluation of ΔF from this equation gave results shown in Table 41.

TABLE 41

FREE ENERGY OF UO_2 OXIDATION BY H_2O_2 TO UO_3

Reaction	$-\Delta F$ in kcal/mole	
	300°K	400°K
(27) $UO_2 + H_2O_2\ (liq) \rightarrow UO_3 + H_2O\ (liq)$	57.5	57.2
(28) $UO_2 + H_2O_2\ (aq) \rightarrow UO_3 + H_2O\ (liq)$	54.3	
(29) $U_3O_8 + H_2O_2\ (liq) \rightarrow 3UO_3 + H_2O\ (liq)$	51.0	51.0
(30) $U_3O_8 + H_2O_2\ (aq) \rightarrow 3UO_3 + H_2O\ (liq)$	47.8	

In the experiments made at Columbia University (SAM Columbia 4,6, 13,14) on oxidation of UO_2 to UO_3 by hydrogen peroxide, H_2O_2-solution was passed at 150°C under pressure through the oxide collected on a fritted glass plate. The oxidation product contained considerable amounts of uranium peroxide, $UO_4 \cdot aq$. Addition of PbO slowed down the oxidation to UO_3, without preventing it, and markedly reduced the proportion of uranium peroxide formed. In the presence of 4 per cent PbO, for example, less than 0.5 per cent $UO_4 \cdot xH_2O$ was formed. Equivalent amounts of PbO_2, Pb_3O_4 and PbO had approximately the same inhibiting effect. No pH effect on the decomposition of H_2O_2 by UO_2 was observed between pH 6.4 and 9.4. No effect of H_2O_2 concentration on the rate of oxidation of UO_2 was noticed at 100°C with moderate agitation.

Oxidation of U_3O_8 suspensions in water by H_2O_2 also was studied at Columbia University (SAM Columbia 14). A preliminary series of experiments was made at 100°C with moderate agitation. Various U_3O_8 preparations were oxidized with different ease. 0.4 to 4 per cent PbO prevented the oxidation. U_3O_8 proved to be a catalyst for decomposition of

H_2O_2; U_3O_8 + PbO catalyzed slightly better than U_3O_8 alone. In the presence of OsO_4, U_3O_8 was rapidly oxidized by H_2O_2. 0.4 per cent PtO (reduced) did not stabilize U_3O_8 markedly. OsO_4 and PtO are not much better catalysts for H_2O_2 decomposition than U_3O_8 + PbO. No effect of particle size or pH (5-9) on the rate of oxidation could be observed.

In a second series of experiments it was found that the amount of PbO required to stabilize a U_3O_8 slurry in presence of H_2O_2 increases with agitation and with the length of the experiment, and that the rate of oxidation increased with the U_3O_8 concentration in a slurry.

In a third series of experiments it was found that 4 per cent PbO decreases oxidation at 100°C and 150°C by 0.4 M H_2O_2, but oxidation remains marked at 200°C. The decomposition of H_2O_2 was catalyzed by U_3O_8 + 4 per cent PbO at all three temperatures used; U_3O_8 alone caused no catalytic decomposition at 100°C. There was very little oxidation by 0.004 M H_2O_2, even in pure U_3O_8, at temperatures up to 200°C.

(b) Formation of UO_3 Hydrates by Oxidation of UO_2 and U_3O_8.

Ebelmen (1842b) asserted that U_3O_8 hydrate (obtained by photochemical decomposition of uranyl oxalate) goes over into $UO_3 \cdot 2H_2O$ when dried in air; Aloy (1900,1901) found, however, that this procedure leads to the formation of $UO_3 \cdot H_2O$.

Oechsner de Coninck (1908) obtained $UO_3 \cdot 2H_2O$ by the action of warm H_2O_2 on UO_2 and $UO_3 \cdot H_2O$ (with only a little dihydrate) by the same reaction at room temperature.

Drenckman (1861) obtained $UO_3 \cdot 2H_2O$ by heating a mixture of U_3O_8 and $KClO_3$ and then washing with boiling water.

Aloy (1900,1901a) recommended the preparation of $UO_3 \cdot H_2O$ by oxidation of U_3O_8 hydrates in air. This procedure gives amorphous monohydrate at room temperature and a crystalline form (rhombic platelets and prisms) at 100°C. Pure $UO_2 \cdot 2H_2O$ can also be used but its oxidation is much slower than that of $U_3O_8 \cdot aq$.

(c) <u>UO_3 - Preparation by Decomposition of $UO_4 \cdot 2H_2O$</u>. A widely used method of preparation of UO_3 and of other lower uranium oxides uses uranium peroxide as starting material. Uranium peroxide hydrate $UO_4 \cdot aq$ is easily obtained by precipitation with H_2O_2 from any uranium (IV) or uranyl salt solution.

The de-oxygenation temperatures of $UO_4 \cdot aq$ depend not only on oxygen pressure but also on H_2O pressure (since the free energy of de-oxygenation changes with the water content). The data on the rate and temperature of decomposition are numerous but not systematic, and the results of various observers are not in complete agreement.

Fairley (1877a), Sieverts and Müller (1928) and Rosenheim and Daehr (1929a) all stated that no loss of oxygen occurs in air at 100°C even after several hours. Hüttig and v. Schroeder (1922) found, on the other hand (comp. section 3.4), that under 15 mm H_2O pressure one-half atom oxygen is lost at 54°C and another one-half atom at 163°C (cf. Fig. 9). Alibegoff (1886) observed that decomposition began at 115°C in an oxygen stream and became strong at 140°C.

Brunck (1895) observed no loss of oxygen in a stream of carbon dioxide up to 150°C. Rosenheim and Daehr (1929) observed complete decomposition to orange UO_3 at 187°C.

Biltz and Müller (1927) prepared pure UO_3 by decomposing small quantities of $UO_4 \cdot 2H_2O$ in a stream of oxygen for one-half to one hour at 350°C-400°C. By heating the same peroxide to 600°C in nitrogen stream, or to 800°C in air, they obtained U_3O_8.

According to Columbia University observations (SAM Columbia 4) $UO_4 \cdot 2H_2O$ is converted to $UO_3 \cdot 2H_2O$ by heating to above 110°C and to red-orange, "active" UO_3, by heating to 250°C in oxygen or air.

According to the same laboratory (SAM Columbia 7,11) solid $UO_4 \cdot 2H_2O$ begins to lose oxygen (under 1 atm partial pressure of oxygen) a little below 100°C. The decomposition is complete in three hours at 200°C and is 75 per cent complete in thirteen hours at 143°C. The temperature dependence of the rate of decomposition indicates a heat of activation of 28 kcal/mole. The decomposition of $UO_4 \cdot 2H_2O$ was also studied at Columbia in an aqueous slurry in sealed pyrex glass tube. At 100°C 2 per cent was decomposed after twenty-eight hours, 40 per cent after four hundred and eight hours, 50 per cent after four hundred and eighty hours. At 185°C 70 per cent was decomposed after one-half hour, 99 per cent in one hour. The activation evergy is 32 ± 5 kcal/mole; no decision as to the order of reaction could be made.

The decomposition appears to be irreversible under the conditions used in these experiments; the final oxygen pressure in the sealed tube experiment at 133°C was as high as 37 atm but the decomposition was nevertheless complete.

At Brown University (Brown 1,3) it was observed that a complex decomposition involving loss of oxygen and water occurs in the region 125°C-175°C. At 250°C-300°C complete conversion to UO_3 takes place. At 125°C-130°C after twenty-four hours an intermediate oxide is obtained which can be completely dehydrated to $UO_{\sim 3.5}$ (cf. p. 19).

According to later Brown data (Brown 5) complete conversion of $UO_4 \cdot aq$ to UO_3 can be achieved in air in three hours at 250°C-350°C; above 400°C, U_3O_8 is slowly formed (according to p. 98 , UO_3 is stable in air up to about 400°C). In vacuum water is lost at 50°C-100°C until $UO_4 \cdot 2H_2O$ remains; above 125°C both water and oxygen are lost at a measurable rate, and anhydrous trioxide is formed just above 325°C.

This method was used at Berkeley (UCRL 7) on a large scale. UO_4 was precipitated from $UO_2(NO_3)_2$, washed by decantation, filtered through a Buchner funnel, the cake dried, powdered and decomposed at 200°C until most water was driven off, then the temperature was raised to 325°C for one-two hours.

According to these observations, $UO_4 \cdot aq$ can be completely decomposed to UO_3 in oxygen in three hours at 250°C-300°C; in vacuum, anhydrous UO_3 can be obtained just above 325°C.

4.7 Formation of $UO_{3.5}$ from $UO_4 \cdot 2H_2O$.

As mentioned on p. 108 an anhydrous uranium "peroxide" with a composition close to $UO_{3.5}$ was obtained at Brown University (Brown 1,3,5) by first decomposing $UO_4 \cdot 2H_2O$ at 125°C-130°C for twenty-four hours (until UO_4 was about one-half decomposed to UO_3) and then raising the temperature to 325°C. The product liberates oxygen on contact with water or acids (cf. p. 19).

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Similar "peroxides" were obtained from ammonium uranate (cf. p. 19).

4.8 Formation of $UO_4 \cdot aq$ by Oxidation of Lower Oxides

The above described Columbia University observations on the decomposition of $UO_4 \cdot aq$ in sealed tubes (SAM Columbia 11) indicate that oxidation of UO_2 by oxygen to $UO_4 \cdot aq$ is unlikely to occur even under very high pressure of oxygen. As mentioned on p. 107, in some experiments at 133°C the final oxygen pressure in the tube was as high as 30 atm but this did not prevent complete decomposition.

Hydrogen peroxide can oxidize UO_2 or U_3O_8 beyond the UO_3-stage. The oxidation of UO_3 by hydrogen peroxide to $UO_4 \cdot aq$ was first noted by Sieverts and Müller (1928). Solid UO_3 was left standing with 50cc 30 per cent H_2O_2 for twelve hours at room temperature in neutral solution, decanted, and then washed first with a little H_2O and then repeatedly with alcohol and ether. It was found to be converted into a light yellow peroxide (p.   ). Oxidation of UO_3-water slurries by H_2O_2 was studied at Columbia University (SAM Columbia 14). Appreciable oxidation was found at 100°C with moderate agitation, even in the presence of 0.4 per cent PbO; but oxidation became negligible in the presence of 4 per cent PbO. (Cf. above, p. 104.)

5. Conversion of Other Uranium Compounds to Oxides.

5.1 Conversion of U(III) Compounds to UO and UO_2.

5.2 Conversion of U(IV) Compounds to UO_2 and U_3O_8.

5.3 Conversion of U(VI) Compounds to Oxides.

(a) Conversion of Uranyl Salts to UO_2.

(b) Conversion of Uranates to UO_2.

(c) Conversion of Uranyl Salts to U_3O_8.

(d) Conversion of Uranates to U_3O_8.

(e) Conversion of Uranyl Salts to UO_3.

(f) Conversion of Uranyl Salts to UO_3 Hydrates.

(g) Conversion of Uranates to UO_3 and $UO_{3.5}$ (?).

(h) Conversion of Uranyl Salts to $UO_4 \cdot aq$.

5. CONVERSION OF OTHER URANIUM COMPOUNDS TO OXIDES

5.1 Conversion of U(III) Compounds to Oxides. In Britain (British 1) x-ray diffraction lines of UO were observed in an oxidation product of uranium trifluoride. This product was formed when a leak occurred in an apparatus in which pure uranium trifluoride was being heated at 1200°C. Previously, the

same x-ray pattern was observed in a product, obtained by heating UF_5 to 1000°C for seven days, which analyzed 92.8 per cent uranium and 0.1 per cent fluorine and apparently consisted mainly of UO_2 + UO.

Uranium hydride burns to UO_2 and H_2O in oxygen or air (MP Ames 1). It reacts with liquid water, sometimes explosively, as well as with water vapor forming UO_2 and hydrogen.

5.2 Conversion of U(IV) Compounds to UO_2 and U_3O_8. Several methods for the conversion of UF_4 to fluorine-free U_3O_8 were developed at Ames (MP Ames 12,13), at the Tennessee Eastman Company (CEW-TEC 6) and at Brown University (Brown 2). For the description of these methods, see Chapter 12 (Uranium Fluorides).

When U^{IV} chlorides or double salts such as Na_2UCl_6 are heated in water vapor, they are hydrolyzed with the formation of UO_2. Air must be excluded to prevent oxidation to U_3O_8. These

reactions will be discussed in Chapter 14 dealing with the properties of uranium chlorides.

Ebelmen (1842) and Hermann (1861) obtained UO_2 by heating uranium (IV) sulfate, $U(SO_4)_2$, in a stream of hydrogen, and also by heating the same compound to 200°C with K_2S_5 and washing the product with water.

5.3 Conversion of U(VI) Compounds to Oxides.

(a) Conversion of Uranyl Salts to UO_2. Uranyl salts can give UO_2 either by straight thermal decomposition, e.g.,

$$(36) \qquad UO_2Br_2 \longrightarrow UO_2 + Br_2 ,$$

or by reduction, e.g.,

$$(37) \qquad UO_2Cl_2 + H_2 \longrightarrow UO_2 + 2HCl ,$$

or by conversion to UO_3, combined with thermal decomposition of the latter, e.g.,

$$(38) \qquad UO_2Cl_2 + CaO \longrightarrow UO_3 + CaCl_2$$

$$(39) \qquad UO_3 \longrightarrow UO_2 + \tfrac{1}{2}O_2$$

(see, however, p. 85 about the difficulties of complete reduction of UO_3 to UO_2).

Oechsner de Coninck (1902) obtained "brick-red UO_2" by thermal decomposition of uranyl bromide, UO_2Br_2, in air. In contrast to the product obtained from UO_2Cl_2 (see below) this material did not re-oxidize to U_3O_8 in air. By heating in hydrogen the brick-red product was converted to black UO_2. This description makes one wonder whether the brick-red oxide might not have been UO_3 rather than UO_2.

Oechsner de Coninck also prepared UO_2 by reducing uranyl chloride, UO_2Cl_2 (1902), or uranyl sulfate, UO_2SO_4 (1903), with hydrogen, as well as by heating UO_2Cl_2 with magnesium or aluminum powder (1909). Reduction with magnesium was also described by Mallinckrodt investigators (Mallinckrodt 1). With potassium or sodium as reductants alkali uranates are likely to be formed together with the dioxide (Oechsner de Coninck, 1909). The same author found that UO_2 (black or brownish red) can also be produced from UO_2Cl_2 by heating with CaO or $Ba(OH)_2$ in the absence of air.

Arfvedson (1822b, 1824) obtained UO_2 by igniting $2KCl \cdot UO_2Cl_2$ in dry hydrogen and leaching the KCl with water.

The "roasting" of uranyl fluoride, UO_2F_2, at 800°C in a rotary reactor was described by the Tennessee Eastman Company (CEW-TEC 6).

Milbauer (1904) converted uranyl sulfide to U_3O_8 and SO_2 by prolonged ignition in air.

Ipatiev and Muromtsev (1930) reduced uranyl nitrate solution to UO_2 at a temperature as low as 360°C by treatment for five days with hydrogen under a pressure of 50-80 kg/cm^2.

When organic uranyl salts are ignited, the anion itself may act as reductant. Thus, Oechsner de Coninck (1908, see Müller, 1915) obtained black pyrophoric UO_2 by dry distillation of uranyl formate, $UO_2(COOH)_2$. He also found (1912) that UO_2 is formed when a suspension of uranyl formate in methanol is allowed to stand in diffuse light for three months. Berzelius (1824) prepared UO_2 by igniting uranyl oxalate, $UO_2(C_2O_4)_2$, in absence of air. Peligot (1842) and Ebelmen (1842) recommended calcining $UO_2(C_2O_4)_2$ in dry hydrogen. Peligot's product was first black, then brown and pyrophoric; Ebelmen's product was copper-red, lustrous, crystalline, and was more stable the higher the temperature of its preparation. It should be noted that Rammelsberg (1843a) found UO_2, obtained from oxalate, always to contain some carbon.

(b) Conversion of Uranates to UO_2. Wöhler (1842) treated $(NH_4)_2U_2O_7$ solution in hydrochloric acid with excess NH_4Cl and NaCl, evaporated and melted the residue. After extraction of the melt with water, black UO_2 crystals were left behind (for discussion whether the product contains nitrogen, see Uhrlaub (1859) and Hillebrand (1893)).

According to Hofmann and Höschele (1915) pure UO_2 in well-formed black, lustrous cubes can be obtained by melting one part Na_2UO_4 with four parts anhydrous $MgCl_2$. Parsons (1917) described a technical method of converting $Na_2U_2O_7$ to UO_2 by melting with NaCl and charcoal which permits recovery of V_2O_5 contained in the uranate. This reaction finds some application in the extraction of uranium from ores.

(c) Conversion of Uranyl Salts to U_3O_8. All soluble uranyl salts can be converted to oxide by precipitating with alkali, treating the precipitate with ammonia and decomposing the ammonium diuranate (cf. below), or by precipitating $UO_4 \cdot 2H_2O$ by H_2O_2 and decomposing the peroxide.

Uranyl salts of volatile or unstable acids can also be converted to U_3O_8 directly by heating. Moissan (1896) obtained U_3O_8 by igniting uranyl nitrate in a porcelain crucible. McCoy and Ashman (1908) converted pure uranyl nitrate to orange UO_3 by heating below red heat and then to U_3O_8 by raising the temperature to 700°C. Zimmermann, Alibegoff and Krüss (1886) prepared pure U_3O_8 by decomposing pure uranyl nitrate, or oxalate (also hydroxide or peroxide), reducing the product with hydrogen to UO_2 and re-oxidizing to U_3O_8 in pure oxygen. According to Ipatiev and Muromtsev (1930) heating of 10 per cent uranyl nitrate solution to 360°C under 50-80 kg/cm^2 initial hydrogen pressure leads in two days to black

U_3O_8 (longer treatment gives UO_2, cf. p. 113).

Péligot (1842) and later Oechsner de Coninck (1901,1903) observed that thermal decomposition of uranyl salts gives, together with green U_3O_8, a black oxide which they considered to be U_2O_5; this was contradicted, among others, by Zimmermann, Alibegoff and Krüss (1886); the existence of U_2O_5 is in general doubtful (cf. p. 13).

(d) Conversion of Uranates to U_3O_8. A commonly used method of preparation or purification of U_3O_8 is by thermal decomposition of ammonium diuranate, $(NH_4)_2U_2O_7$ (obtained from uranyl nitrate by precipitation with NH_4OH):

$$9(NH_4)_2U_2O_7 \longrightarrow 2N_2 + 14NH_3 + 6U_3O_8 + 15H_2O \tag{40}$$

Pierlé (1919) recommended ignition of ammonium diuranate in air as a good method of preparation of U_3O_8. Giolitti and Tavanti (1908) purified U_3O_8 by dissolution in HNO_3, repeated precipitation with NH_4OH and decomposition of pure ammonium diuranate. At Brown University (Brown 6) ammonium diuranate was washed, dried at 130°C in air and calcined for four hours at 350°C to give U_3O_8. In Britain (British 5), $(NH_4)_2U_2O_7$ was precipitated from uranyl nitrate solution (previously purified from Fe), washed with hot water, dissolved in hydrochloric acid, purified by precipitation of impurities with hydrogen sulfide, again converted to ammonium diuranate, and then to U_3O_8 by ignition at 700°C in electric furnace. In another procedure (British 6) UF_6 was converted to $(NH_4)_2U_2O_7$ by first converting it with NaOH to $Na_2U_2O_7$, dissolving the precipitate in HNO_3 and re-precipitating with NH_4OH, after which U_3O_8 was obtained by ignition at 600°C in air with an over-all yield of 99 per cent.

At the Tennessee Eastman Company (CEW-TEC 6) $(NH_4)_2U_2O_7$ was roasted to U_3O_8 at 700°C in a rotary reactor.

(e) Conversion of Uranyl Salts to UO_3. In the preparation of UO_3 by thermal decomposition of $UO_2(NO_3)_2$ difficulties arise as a result of the necessity of raising the temperature high enough to ensure complete decomposition of the nitrate, and of the requirement that the temperature be kept low to prevent decomposition of UO_3 to U_3O_8. Arfvedson (1822, 1824a, 1825) maintained that the establishment of such conditions is impossible and that nitrate cannot be fully destroyed before some of the oxide is converted to U_3O_8. Péligot (1844), on the other hand, thought he could convert uranyl nitrate to nitrogen-free UO_3 by calcining at 250°C. Mixter (1912a) used a temperature of 400°C, while Lebeau (1912), Jolibois and Bossuet (1922) and Hüttig and v. Schroeder (1922a) found 350°C insufficient and 500°C satisfactory. Lebeau recommended heating in an oxygen stream to avoid formation of U_3O_8.

De Forcrand (1915a) recommended low temperatures (290°C-300°C) since he considered the dark red oxides obtained at 500°C-600°C as "polymerization products" of UO_3 of unknown degree of polymerization (which may be taken to mean different allotropic modifications of UO_3, cf. p. 42).

At Columbia University (SAM Columbia 2) pure UO_3 was prepared by ignition of uranyl nitrate hydrate at 300°C. Long, Jones and Gordon (Nat. Bur. Standards 4) heated UO_2 nitrate for eight hours at 300°C in a closed furnace in order to maintain an oxidizing atmosphere (NO_2). No impurities capable of reducing $KMnO_4$ were found in the product and no nitrate could be detected by the H_2SO_4 + $FeSO_4$ test.

Ebelmen (1842d) converted double ammonium uranyl carbonate to UO_3

by prolonged heating at 300°C. Brunck (1895) recommended that UO_3, obtained by calcination of uranyl nitrate at 300°C and still containing some nitrogen, be purified by conversion to ammonium uranyl carbonate which is then decomposed by prolonged heating to 300°C in air.

Oechsner de Coninck (1901,1908) prepared UO_3 from $UO_2SO_4 \cdot 3H_2O$ by heating to red heat.

(f) *Conversion of Uranyl Salts to UO_3-Hydrates by Hydrolysis or Electrolysis.* The hydrates $UO_3 \cdot H_2O$ and $UO_3 \cdot 2H_2O$ (or intermediate solid solutions) can be obtained by hydrolysis or electrolysis of uranyl salt solutions. According to the data given on p. 54, one may expect $UO_3 \cdot 2H_2O$ to be formed below 60°C and $UO_3 \cdot H_2O$ above 100°C; intermediate solid solutions (or the sesquihydrate, if it exists) should arise in the intermediate range of temperatures. Experimental results are not so clear-cut.

Ebelmen (1842b) and Drenckmann (1861) claimed to have obtained $UO_3 \cdot 2H_2O$ by prolonged boiling of ammonium uranyl carbonate solution. Riban (1881,1882) obtained crystalline $UO_3 \cdot H_2O$ (hexagonal prisms) by heating a 2 per cent uranyl acetate solution to 175°C in a sealed tube for one hundred hours in vacuo. Zehenter (1900) found heating to 140°C-150°C for eight hours to be sufficient. According to this author refluxing a sodium uranyl acetate solution also gives $UO_3 \cdot H_2O$ slightly contaminated by Na (rather than a sodium polyuranate). The product consists of sulfur-yellow, lustrous, hexagonal tablets.

In connection with the last described results it should be remembered that hydrolysis of organic uranyl salts may lead to reduction and thus to the formation of hydrates of UO_2 or U_3O_8 rather than of UO_3 (see p. 113).

Hydrolysis of uranyl salts of mineral acids always leads to UO_3 hydrates. The formation of $UO_3 \cdot H_2O$ by evaporation of uranyl nitrate solution and heating was first observed as early as 1843 by Malaguti. Ipatiev and Muromtsev (1930) obtained crystalline $UO_3 \cdot H_2O$ in the form of transparent prisms by hydrogenating under high pressure at 300°C a solution of uranyl nitrate in nitric acid.

Berzelius (1845) found that the monohydrate also can be obtained by the hydrolysis of solid hydrated uranyl nitrate (by heating on a sand bath); Oechsner de Coninck (1911) found that careful ignition of $UO_2(NO_3)_2 \cdot aq$, washing with warm water and drying gives pure orange $UO_3 \cdot H_2O$ without traces of yellow $UO_3 \cdot 2H_2O$. Hydrolysis explains also the formation of $UO_3 \cdot H_2O$ by reaction of uranyl salt solutions with hydrocyanic acid, according to Fischel (1889).

As mentioned in section 3 Smith (1879,1880) found that electrolytic decomposition of uranyl salt solutions gives a U_3O_8 hydrate. A yellow $UO_3 \cdot H_2O$ is supposedly produced first but is later converted into a black hydroxide ($U_3O_8 \cdot 2H_2O$?). Oechsner de Coninck and Camo (1901b) also obtained $UO_3 \cdot H_2O$, together with $UO_3 \cdot 2H_2O$, by electrolysis of uranyl nitrate. Pierlé (1919) obtained the $UO_3 \cdot H_2O$ by electrolysis of uranyl acetate solution at room temperature with a current density of 0.1 amp/(100 sq cm). The "black oxide" obtained by prolonged electrolysis, which was interpreted by Smith as $U_3O_8 \cdot 2H_2O$, has according to Pierlé the composition $U_3O_{10} \cdot 2H_2O$.

The electrolytic deposition of U_3O_8 hydrates on uranium electrodes was also studied by Francis and Tcheng-Da-Tchang (1935) and Francis (1935).

(g) <u>Conversion of Uranates to UO_3 and $UO_{3.5}$</u>. In order to convert

$(NH_4)_2U_2O_7$ to UO_3 without further decomposition to U_3O_8 one has to use low temperatures. Ebelmen (1842d) obtained UO_3 by prolonged heating to 300°C; Brunck (1895) noted that UO_3 so obtained still contains nitrogen and recommended purification by conversion to ammonium uranyl carbonate and its subsequent decomposition (cf. above). Goldschmidt and Thomassen (1923b) heated $(NH_4)_2U_2O_7$ to 230°C for sixteen hours and then to 260°C-270°C for twenty hours; the product was stated still to contain some water.

Brown University observers (Brown 4) confirmed the fact that UO_3 prepared by low temperature decomposition of $(NH_4)_2U_2O_7$ contains some ammonia which cannot be removed simply by heating without causing conversion to U_3O_8; preparation with $UO_4 \cdot 2H_2O$ was therefore found more reliable. Similar observations were made at Clinton Laboratory (Clinton 1). In a later report (Brown 6) the Brown group reported the preparation of UO_3 from $(NH_4)_2U_2O_7$ by drying in air at 130°C, and calcination at 350°C for four hours, followed by washing with water. The hydrated trioxide obtained in this way is then re-calcined for four hours at 350°C to obtain anhydrous UO_3. Bright red UO_3 was obtained by ignition of ammonium diuranate also at the UCRL (UCRL 6). In a later report from the same laboratory (UCRL 8) $(NH_4)_2U_2O_7$ was calcined at 500°C.

As mentioned on p. 19 Brown University observers (Brown 2) found that if ammonium diuranate is decomposed in a rapid stream of oxygen and the temperature is gradually increased from 250°C to 550°C, the evolution of ammonia and water (which occurs at 250°C-350°C) is followed by the formation of a red powder which appears to be stable at high temperatures and analyzes between $UO_{3.14}$ and $UO_{3.88}$. This product appears to be a peroxide or rather a "moloxide"; it releases its "excess" oxygen on contact with water or acid. It may be a mixture of UO_3 with $UO_{3.9}$, the anhydrous "peroxide" obtained at Brown from $UO_4 \cdot 2H_2O$ (cf. p. 19).

(h) *Conversion of Uranyl Salts to $UO_4 \cdot aq$.* All soluble uranyl salts are converted to $UO_4 \cdot aq$ by hydrogen peroxide. The same is true of U(IV) salts which are probably first oxidized to U(VI) salts and then to uranium peroxide. This important reaction will be dealt with in the second part of this treatise (Ch.).

6. Conversion of Oxides to Other Uranium Compounds

6.1 Halogenation

- (a) Fluorination
- (b) Chlorination
- (c) Bromination

6.2 Miscellaneous Reactions

- (a) Conversion to Sulfides
- (b) Conversion to Carbides
- (c) Conversion to Uranates
- (d) Conversion to Uranium (IV) and Uranyl Salts

6. CONVERSION OF OXIDES TO OTHER URANIUM COMPOUNDS

6.1 Conversion of Uranium Oxides to Halides and Oxyhalides

(cf. Chapters 12,14,15,16).

(a) Fluorination. UO_2. Uranium dioxide can be converted to UF_4 by the action of gaseous hydrogen fluoride, fluorinated hydrocarbons ("freons") and by reaction with $NH_4F \cdot HF$. These reactions are described in detail in Chapter 12.

According to Los Alamos observers (HP Los Alamos 1) UO_2 does not react with molten NaF or BaF_2, but reacts with other metal fluorides (cf. Chapter 12).

U_3O_8. According to Bolton (1866) U_3O_8 reacts with aqueous hydrofluoric acid to give soluble UO_2F_2 and insoluble UF_4.

UO_3. According to Gore (1869) UO_3 is soluble in pure anhydrous liquid hydrogen fluoride, probably with the formation of UO_2F_2.

(b) <u>Chlorination</u>. <u>UO_2</u>. UO_2 is insoluble in dilute or concentrated, cold or hot hydrochloric acid (Arfvedson, 1822a, 1824; Péligot, 1842). Hot fuming HCl converts UO_2 slowly into green UCl_4 (Hoffman and Höschele, 1915). Hydrogen chloride gas does not attack UO_2 even at high temperatures (Péligot, 1842).

UO_2 can be chlorinated by many inorganic or organic chlorinating agents. Among these are S_2Cl_2, $CCCl_2$, CCl_4 and C_3Cl_6 (see Chapter 14 for detailed discussion and bibliography).

The conversion of UO_2 to uranyl chloride, UO_2Cl_2, can be achieved by means of dry chlorine at red heat (Péligot, 1842). According to Brown University observers (Brown 4) brown UO_2 is converted to UO_2Cl_2 also when used as anode in the electrolysis of hydrochloric acid.

In the same laboratory (Brown 2) UO_2 was converted to anhydrous $UOCl_2$ by dissolution in excess molten UCl_4 at 600°C under dry nitrogen.

<u>U_3O_8</u>. This oxide reacts only very slowly with dilute hydrochloric acid, even at elevated temperatures, particularly after calcination (Arfvedson, 1822, 1824a). Reaction with concentrated hydrochloric acid

is more rapid; heating with HCl (sp. w. 1.135) in carbon dioxide atmosphere in a closed tube from 180°C-200°C leads to rapid conversion to a green liquid (Zimmermann, Alibegoff and Krüss, 1886).

In the presence of oxidizing agents, e.g., HNO_3, hydrochloric acid fairly readily dissolves U_3O_8 to UO_2Cl_2 (British 7).

Black, commercial U_3O_8 was found by Kangro and Jahn (1933) to be attacked by chlorine at 900°C, giving yellow crystals of UO_2Cl_2.

Bourion (1910) converted U_3O_8 to UCl_4 by heating to 230°C-250°C with S_2Cl_2. Rosenheim and Kelmy (1932) converted U_3O_8 to UCl_4 and UO_2Cl_2 by the action of $COCl_2$ at 500°C. According to Michael and Murphy (1910) heating of U_3O_8 with CCl_4 in closed tubes leads to the formation of dark red crystals of UCl_5 which upon further heating readily dissociate into UCl_4 and chlorine. Venable and Jackson (1919-1920) gave 360°C as the temperature of chlorination of U_3O_8 by CCl_4.

The chlorination of U_3O_8 with CCl_4, $SOCl_2$ and other similar chlorinating agents, in the gas phase or in the liquid phase, has acquired considerable importance and is discussed in detail in Chapter 14.

UO_3. Gore (1865) stated the UO_3 changes its color to a lighter yellow in hydrogen chloride gas. It does not dissolve in hydrochloric acid but the residue is soluble in water. No conversion of UO_3 to UCl_4 could be obtained at Purdue (Purdue 1) by anhydrous HCl up to 400°C. Action of hydrogen chloride in C_2H_5OH on UO_3 apparently gave UO_2Cl_2 but no UCl_4.

According to Brown University investigators (Brown 1,4) gaseous HCl reacts under atmospheric pressure with UO_3 when the latter is hydrated or moisture is present to form hydrated UO_2Cl_2.

The reaction of UO_3 with aqueous hydrochloric acid will be discussed in Section 6.2(d) of this chapter.

Chlorination of UO_3 with S_2Cl_2 was carried out at Brown University (Brown 7). The UO_3 obtained by decomposition of peroxide was found to be most reactive. 99.5 per cent of the UO_3 taken was converted to UCl_4 at the end of one hour heating to 138°C. The reaction can be written as

$$2UO_3 + 4S_2Cl_2 \longrightarrow 2UCl_4 + 5S + 3SO_2$$

At Purdue University (Purdue 1) UO_3 (prepared by decomposition of $UO_4 \cdot 2H_2O$) was nearly 100 per cent converted to UCl_4 by one hour treatment with $SOCl_2$ at 350°C. With UO_3, obtained by thermal decomposition of $UO_2(NO_3)_2 \cdot aq$, caking occurred and conversion was incomplete. No conversion to UCl_4 was obtained with SO_2Cl_2 up to 400°C.

At the Tennessee Eastman Company (CEW-TEC 8) 95 per cent recovery has been achieved in chlorination of UO_3 with $SOCl_2$ vapor at 290°C-300°C, the yield varying directly with the purity of the reagent. Results with SO_2Cl_2 were poor.

According to Rauter (1892) UCl_4 and UO_2Cl_2 are obtained, together with SiO_2 and Cl_2, when UO_3 is heated to 370°C-380°C for eight hours with $SiCl_4$ in a closed tube.

Chlorination of UO_3 by $CO + Cl_2$ was described by Quantin (1888). The same author also carried out the first chlorination of UO_3 with CCl_4 by heating the oxide to red heat in CCl_4 vapor. Camboulives (1910) found that the reaction of UO_3 with CCl_4 vapor occurs at 360°C and gives UCl_4 and UCl_5. Michael and Murphy (1910) also observed the formation of unstable dark red UCl_5 crystals by heating UO_3 with CCl_4 vapor (with or without Cl_2) in a closed tube.

The liquid phase chlorination of UO_3 by CCl_4 has been intensively studied, and the reader is referred to Chapter 14 for details.

(c) Bromination. UO_2. At the Metallurgical Laboratory (MP Chicago 10) it was found that UO_2 (prepared by reduction of U_3O_8 with hydrogen at 300°C or 900°C) could not be converted to UBr_4 by the action of HBr (even at 800°C) or of CH_3Br (at 550°C). Hermann (1861) obtained UBr_4 by the action of bromine vapor on a mixture of UO_2 and carbon.

U_3O_8. Heating of U_3O_8 in Br_2 vapor or in dry HBr gives a mixture of uranyl bromide and lower oxides (Richards and Merigold, 1902).

Further details on the conversion of the uranium oxides to bromides are to be found in Chapter 15.

6.2 Miscellaneous Reactions.

(a) Conversion of Uranium Oxides to Sulfides and Oxysulfides. Heating UO_2 or U_3O_8 in carbon disulfide vapor leads, according to Hermann (1861), to the formation of the oxysulfide $UO_2 \cdot 2US_2$. A mixture of carbon dioxide and carbon disulfide showed no reaction with UO_2 but reduced U_3O_8 and UO_3 at a red heat to UO_2 (cf. p. 94).

According to Ames observations (MP Ames 14) UO_2 gives $UO_2 \cdot 2US_2$ with carbon disulfide at 900°C. The Berkeley observations (MP Berkeley 4) on the conversion of uranium oxides to US_2 and UOS by reaction with hydrogen sulfide, and to U_2S_3 by subsequent decomposition of US_2 are reported in section 7.

(b) Conversion of Uranium Oxides to Carbides. Tiede and Birnbräuer (1914) found that UO_2 reacts with carbon in vacuum apparently at temperatures as low as 1600°C forming a uranium carbide. Greenwood (1908) found that the reaction of UO_2 with carbon begins in an electric vacuum furnace at about 1490°C (at this temperature the formation of CO can be deduced from increase in pressure). Heusler (1926) studied quantitatively the equilibrium:

$$(45) \qquad UO_2 + 4C \rightleftharpoons UC_2 + 2CO$$

between 1480°C and 1800°C. The equilibrium carbon monoxide pressure is 18 mm Hg at 1480°C and reaches one atm at 1800°C. Equation

$$(46) \qquad \log p_{(CO)} = -19{,}100/T + 12.09$$

represents the data approximately, but deviations indicate the ΔH must change appreciably in the investigated temperature interval. The average ΔH value is 87.3 kcal/mole.

For more details on these reactions, seeChapter 9.

(c) Conversion of Uranium Oxides to Uranates and Peruranates by Reaction with Metal Oxides, Peroxides and Salts. In contrast with UO_2, which is a basic oxide, UO_3 is amphoteric giving rise both to the uranyl salt series UO_2X_2 and to the uranate and polyuranate series X_2UO_4,

$X_2U_2O_7$, etc. U_3O_8 ($=UO_2 + 2UO_3$) can be partially converted to uranates, e.g., by reaction with metal oxides:

$$U_3O_8 + 2BaO \longrightarrow 2BaUO_4 + UO_2 \tag{47}$$

BaO reacts vigorously with U_3O_8 at or above 330°C, cf. Balarew (1924); the conversion may be complete if an oxidant is present, e.g.,

$$U_3O_8 + 6KClO_4 \longrightarrow 3K_2UO_4 + 3Cl_2 + 10\ O_2 \tag{48}$$

According to Fowler and Grant (1890) and Hodgkinson and Lowndes (1888,1889) U_3O_8 reacts with solid $KClO_4$ at 390°C with liberation of oxygen and chlorine.

With UO_3, $KClO_4$ gives potassium uranate with liberation of chlorine (Brunck, 1895).

Another reaction of the same type is the conversion of UO_2, U_3O_8 and UO_3 to sodium uranate by solid sodium peroxide. This reaction was mentioned in section 4.1, p. 71 in connection with Mixter's determination of the heats of formation of the various uranium oxides.

According to Mixter (1912) Na_2UO_4 is formed by heating uranium oxides with Na_2O_2 in the calorimetric bomb. The measured heat effects were *

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* Mixter "experimental" values are calculated for the neutralization of U_3O_8 and UO_3 by $Na_2O + Na_2O_2$ in appropriate proportions by assuming a heat effect of 19.4 kcal for the decomposition of Na_2O_2:

$$Na_2O_2 \longrightarrow Na_2O + \tfrac{1}{2}O_2 \quad -19.4\ \text{kcal}$$

(49) $UO_2 + Na_2O_2 \longrightarrow Na_2UO_4 + 110.9$ kcal

(50) $1/3\ U_3O_8 + Na_2O_2 \longrightarrow Na_2UO_4 + 1/3\ O_2 + 82.1$ kcal

(51) $UO_3 + Na_2O_2 \longrightarrow Na_2UO_4 + \frac{1}{2}O_2 + 76.7$ kcal

Mixter finds that no peruranate is formed in the bomb but only normal uranate. However, when the product is extracted with water, it reacts with excess Na_2O_2 and forms peruranate solution. Peruranates must also be formed when UO_2 or U_3O_8 is dissolved in aqueous Na_2O_2 solution (MP Ames 15).

The solubility of UO_2 in aqueous alkaline peroxide solutions was measured at Brown University (Brown 2). The oxide dissolves readily at 25°C-45°C; warm 10 per cent H_2O_2 + 10 per cent K_2CO_3 is most effective. After two minutes shaking of 2 g oxide in 100 cc solvent, the amounts shown in Table 42 were dissolved.

TABLE 42

SOLUBILITY OF UO_2 IN ALKALINE PEROXIDES

Reagent	t°C	per cent UO_2 dissolved
10% H_2O_2 + 10% $(NH_4)_2C_2O_4$	25	35
10% H_2O_2 + 10% $(NH_4)_2CO_3$	25	69
10% H_2O_2 + 10% K_2CO_3	25	46
same	35	83
5% Na_2O_2	45	17

According to the same report warm (45°C) 5 per cent Na_2O_2 is the best solvent for U_3O_8.

The reactions of UO_3 with basic oxides were first studied by Zimmermann (1882a). Tammann and Rosenthal (1926) investigated the reaction of UO_3 with twenty-five metal oxides. Equivalent quantities of UO_3 and metal oxide powders were mixed and heated up twice to 600°C in ten minutes; BeO, La_2O_3, CeO_2 and MoO_2 showed no reaction at all. With Li_2CO_3 ($=Li_2O + CO_2$), Ag_2O, CaCo, BaO, SrO, MgO, ZnO, CdO, HgO, CuO, PbO, CoO, MnO, NiO, Al_2O_3, Cr_2O_3, Fe_2O_3 and V_2O_3 exothermal reactions took place (beginning sometimes as early as at 125°C, e.g. with SrO, sometimes first at 450°C, as with Al_2O_3). The reaction was from ten to ninety per cent complete; from the almost exact equivalence of the quantities of UO_3 and XO used up one can conclude that normal uranate, X_2UO_4, was the only product formed. The fact that a reaction has taken place is usually noticeable from a change in color. The yellow product obtained from CaO and UO_3 becomes green above 505°C and loses oxygen. FeO and SnO reduced UO_3 on heating. (Cf. p. 94 .)

Hedvall (1915) studied the reaction of UO_3 with CoO at 1100°C-1300°C; a yellow crystallized uranate was obtained in some experiments.

At Columbia University (SAM Columbia 5) four different $Bi_2O_3 + UO_3$ compounds were isolated. All were thermally stable and some were not attacked by H_2O_2.

Because of poor solubility of potassium polyuranate, UO_3 is partly converted into this compound when it is dissolved in potassium chloride solution. (See below, section (d).)

According to Hodgkinson and Lowndes (1888,1889) $UO_3 \cdot 2H_2O$ reacts with potassium chlorate evolving chlorine and forming potassium diuranate.

The heat of neutralization of $UO_3 \cdot \frac{1}{2}H_2O$ by NaOH was calculated by Pissarjevsky (1900a) as 17.8 kcal for the reaction

(52) $$2UO_3 \cdot H_2O + 2NaOH \longrightarrow Na_2U_2O_7 + 2H_2O$$

This value was obtained by subtracting the measurement of the heat of decomposition of $Na_2U_2O_7$ by H_2SO_4 to Na_2SO_4 and UO_2SO_4 (44.5 kcal), from the sum of the heats of neutralization of $2UO_3 \cdot H_2O$ and of 2NaOH by $3H_2SO_4$ (2 x 15.35 kcal, measured by Pissarjevsky, cf. p. , and 31.4 kcal respectively).

(d) <u>Conversion of Uranium Oxides to Uranium (IV) and Uranyl Salts</u>. Conversion of uranium oxides to UO_2Cl_2 and UO_2Br_2 was described on p. 123 and 127.

According to Arfvedson (1822a, 1824) and Péligot (1842) UO_2 dissolves in HNO_3 giving a lemon-yellow solution of uranyl nitrate. Very dilute HNO_3 has no effect on UO_2 except causing hydration (Oechsner de Coninck, 1908). UO_2 is easily soluble in concentrated HNO_3 or aqua regia (Raynaud, 1911,1912).

UO_2 can be oxidized to uranyl nitrate also by means of $AgNO_3$ (Smith and Shinn, 1894; Isambert, 1875). $AgNO_3$ in ammonia solution is redused by UO_2 to silver; in neutral solution Ag_2O is precipitated first and then transformed into metallic silver.

Conversion of UO_2 to basic nitrate by the action of NO_2 in the cold (accompanied by heat evolution) was noted by Sabatier and Senderens (1896).

U_3O_8 is dissolved in HNO_3 with the formation of uranyl nitrate and evolution of nitrous oxides. According to British observers (British 4) the conversion of U_3O_8 to uranyl nitrate occurs according to the equation:

$$(53) \qquad 2U_3O_8 + 14HNO_3 \longrightarrow 6UO_2(NO_3)_2 + 7H_2O + NO + NO_2$$

However, this equation does not take into account the formation of complex ions which increase the amount of oxide brought into solution by a given quantity of nitric acid (cf. below). Ignited UO_2 is only slightly soluble in dilute H_2SO_4 but dissolves easily in concentrated acids and completely in boiling concentrated H_2SO_4 (Arfvedson, 1822,1824). U_3O_8 is converted completely to uranyl sulfate and $U(SO_4)_2$ by prolonged heating with concentrated H_2SO_4 (Zimmermann, Alibegoff and Krüss, 1886). U_3O_8 reduces $AgNO_3$ very slowly to metallic silver (Isambert, 1875). UO_3 is soluble in all mineral acids (Lebeau, 1912) giving the corresponding uranyl salts.

The heat of neutralization of UO_3 by diluted HNO_3, i.e., if complex formation is neglected, in the reaction

$$(54) \qquad UO_3 + 2H^+ \text{ (aq)} \longrightarrow UO_2^{++} \text{ (aq)} + H_2O$$

was measured by de Forcrand (1913,1915). He obtained a value of 19.80 kcal/g atom uranium (at 16°C).

The heats of neutralization of $UO_3 \cdot H_2O$ and $UO_3 \cdot 2H_2O$ were found by de Forcrand to be 14.85 kcal and 12.38 kcal/g atom uranium respectively. These values have been used (cf. p. 55) for the calculation of the heats of formation of the two hydrates from UO_3 and H_2O (cf. Table 24). Pissarjevsky (1900) found a value of 15.35 kcal/g atom uranium for the heat of neutralization of $UO_3 \cdot H_2O$ by 2 N H_2SO_4.

Aloy (1896) gave the following values for the heats of neutralization of $UO_3 \cdot H_2O$ by different 0.5 N acids: HCl - 16.8 kcal, HBr - 17.6 kcal, HNO_3 - 16.8 kcal, H_2SO_4 - 19.0 kcal, $H(CH_3COO)$ - 15.0 kcal/g atom uranium.

UO_3 reacts with molten NH_4NO_3 with the formation of uranyl nitrate and liberation of ammonia and water (Audrieth and Schmidt, 1934).

Quantitative determinations of the amount of UO_3 dissolved by a given amount of hydrochloric acid revealed an "extra" solubility which must be attributed to complexing. Table 43 contains some data obtained at the Rockefeller Institute for Medical Research (Rockefeller 1).

TABLE 43

SOLUBILITY OF UO_3 IN HCl(Aq)

[HCl] mole/l	$[UO_3]$ dissociated mole/l	[HCl] mole/l	$[UO_3]$ dissociated mole/l
2.785	2.832	0.03140	0.02986
1.013	0.958	0.01082	0.01138
0.2979	0.2718	0.00298	0.00343
0.09909	0.0900	0.00108	0.00150

These figures indicate a solubility of approximately one mole UO_3 per mole HCl while the reaction

$$(55) \qquad UO_3 + 2HCl \longrightarrow UO_2Cl_2 + H_2O$$

permits the dissolution of only one half mole base per mole acid. Electrometric or conductometric titration of UO_3 with HCl showed a sharp end point at one half mole base per mole acid, confirming the primary formation of uranyl chloride according to equation (55). The "extra" solubility of UO_3 may be due to the complexing with OH^- ions:

$$(56) \qquad UO_2^{++} + UO_3 + H_2O \rightleftharpoons 2UO_2OH^+$$

or to "self-complex ion"

$$(57) \qquad UO_2^{++} + UO_3 \rightleftharpoons UO_3 \cdot UO_2^{++}$$

Conductance and transference measurements cannot distinguish between these two mechanisms but pH measurements appear to favor the second one. The solubility of UO_3 in UO_2^{++} solution, according to equation (56) or (57), can of course not be restricted to chloride solutions but must occur in all uranyl salt solutions. It was measured at Brown University (Brown 1,4) with UO_2Cl_2, $UO_2(NO_3)_2$ and $UO_2(ClO_4)_2$ solutions as solvents. Table 44 shows the results.

TABLE 44

SOLUBILITY OF UO_3 IN UO_2^{++} - SALT SOLUTIONS AT 25°C

Solvent	Equivalents X^- in 1000 g soln	Equivalents UO_3 in 1000 g soln
UO_2Cl_2(Aq)	0.2887	0.5272
	1.453	3.138
	1.780	4.064
	1.927	4.121
	2.299	3.870
	2.392	3.778
	4.004	4.058
	4.415	4.454
	4.550	4.548
	5.747	4.086
$UO_2(NO_3)_2$(Aq)	0.05638	0.1062
	0.1303	0.2290
	0.2878	0.4688
	0.4340	0.6958
	0.7373	1.187
	1.280	1.971
	2.058	2.826
	2.519	3.450
	2.892	2.862
	6.322	1.769
$UO_2(ClO_4)_2$(Aq)	0.09787	0.1627
	0.3764	0.2940
	0.4019	0.6390
	0.7899	1.208
	0.9120	1.368
	1.187	1.717
	1.393	1.974
	1.681	2.246
	2.058	2.568
	2.755	3.206
	3.106	3.028
	4.334	2.088
	5.522	1.401

UO_3 is soluble also in alkali salt solutions. A possible mechanism of this reaction is:

(58) $$2UO_3 + 2KCl + H_2O \longrightarrow K_2U_2O_7{}^{*)} + 2HCl$$

(59) $$2HCl + UO_3 \longrightarrow UO_2Cl_2 + H_2O$$

*) or other polyuranates

The potassium polyuranate precipitates while part of the UO_3 goes into solution as uranyl chloride (Brown 4). Table 45 shows some solubility data.

TABLE 45

SOLUBILITY OF UO_3 IN KCl SOLUTION

KCl mole/liter	t°C	UO_3 dissolved equiv./liter
0.01	room temp.	0.024
0.025	"	0.021
1.0	"	0.054
2.0	"	0.047
3.0	"	0.020
0.362	80	0.036
0.375	80	0.025
0.468	80	0.024
0.571	80	0.028

One measurement of UO_3 solubility in KNO_3 solution was made and gave 0.016 moles UO_3/ℓ in 1.0 N KNO_3 at room temperature (after shaking for twenty-four hours).

The systems to which Tables 44 and 45 refer, in particular $UO_3/HNO_3/H_2O$ and $UO_3/HCl/H_2O$, will be discussed in more detail in the second part of this treatise (Chapter).

CHAPTER 11

Part II. Uranium Sulfides

7. Uranium-Sulfur System

8. Uranium Selenides and Tellurides

7. Uranium-Sulfur System

7.1 Phase Relationships in the Uranium-Sulfur System.

The disulfide, US_2, discovered by Péligot in 1842 is the best known compound in the uranium-sulfur system. Alibegoff described in 1886 the preparation of the sesquisulfide U_2S_3 (by reaction of UBr_3 with hydrogen sulfide) and of the monosulfide US (by reduction of U_2S_3 with hydrogen at red heat), but the correctness of the second statement has been questioned (see below). The monosulfide can be prepared, according to more recent investigations, e.g., by reduction of UOS with carbon at temperatures of the order of 1900°C.

At the Metallurgical Laboratory (MP Chicago 11) samples (prepared by Brewer at Berkeley) with U:S ratio between 1.2 and 1.6 were studied by x-ray analysis. The sample with $S:U \simeq 1.5$ contained a single phase, thus confirming the existence of a sulfide U_2S_3. The sample with $S:U = 1.22$ showed lines of the U_2S_3 phase and those of a cubic phase, US, indicating the absence of other compounds between US and U_2S_3. It is not yet known whether the (orthorhombic) U_2S_3 phase can be converted continuously into the orthorhombic phase US_2(II), or whether a diphasic region separates these two sulfides.

No sulfides derived from U(VI) (and thus analogous to the oxides U_3O_8 and UO_3) are known, but an oxysulfide UO_2S has been described (cf. p.150).

7.2 Physical Properties of Uranium Sulfides.

Crystal Structure and Density.

(a) US. According to Alibegoff (1886a) this is a black amorphous powder but Berkeley observers described the monosulfide as a greyish,

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metallic-looking solid. The crystal structure of uranium monosulfide was studied at Chicago (MP Chicago 2,11,12). It is cubic, face-centered (NaCl-structure) with four uranium atoms in the elementary cell, isomorphous with CeS and ThS (and other sulfides). The lattice constant is

$$a = 5.473 \pm 0.002A.$$

The calculated density is 10.87 g/cc.

According to the same observer x-ray evidence points to the nonexistence of intermediate phases between US and U_2S_3.

(b) $\underline{U_2S_3}$. The sesquisulfide was described by Alibegoff (1886) as grey-black needle-shaped crystals and by Berkeley observers (MP Berkeley 5) as a black crystalline compound. According to Metallurgical Laboratory observations (MP Chicago 1) the U_2S_3 phase is orthorhombic (isomorphous with Th_2S_3 and closely related to Sb_2S_3 and Bi_2S_3). The unit cell contains eight uranium atoms and has the dimensions

$$a_1 = 10.63 \pm 0.02A; \quad a_2 = 10.39 \pm 0.02A; \quad a_3 = 3.88 \pm 0.01A.$$

(c) $\underline{US_2}$. According to Colani (1903,1907) US_2 forms black or steel-gray tetragonal crystals with metallic lustre. According to Metallurgical Laboratory observations, a second orthorhombic form, US_2(II), exists in addition to the tetragonal form US_2(I).

The crystal structure of US_2(I) is, according to Metallurgical Laboratory measurements (MP Chicago 14), tetragonal with the parameters:

$$a_1 = 10.25 \pm 0.05A \quad \text{and} \quad a_3 = 6.30 \pm 0.03A.$$

Assuming that the elementary cell contains ten uranium atoms, the calculated density is 7.54 g/cc.

The orthorhombic form US_2(II) is isomorphous with ThS_2. The space group is Pmnb . The elementary cell contains four uranium atoms. The positions of the atoms are:

4 U-atoms in 4(c), $y_1 = 0.250$, $z_1 = 0.125$
4 S_I-atoms in 4(c), $y_2 = 0.375$, $z_2 = 0.432$
4 S_{II}-atoms in 4(c), $y_3 = 0.465$, $z_3 = 0.820$

The lattice constants are

$$a_1 = 4.22 \pm 0.02A; \quad a_2 = 7.08 \pm 0.04A; \quad a_3 = 8.45 \pm 0.04A.$$
$$\rho = 7.90 \text{ g/cc.}$$

Each uranium atom has nine sulfur atoms as neighbors, the mean U-S distance being 2.91A.

Berkeley observers (MP Berkeley 5) suggested that one of the two US_2 forms described by Zachariasen (the tetragonal one) may be the intermediate compound between US_2 and $US_{1.5}$ mentioned on p. 141 . Because of the analogy between US and ThS, between U_2S_3 and Th_2S_3, and US_2 (orthorhombic) and ThS_2, one may suggest that the intermediate uranium sulfide is U_4S_7, analogous to Th_4S_7. However, the latter compound is hexagonal (according to Zachariasen) while the "extra" uranium sulfide is tetragonal.

<u>Melting Point</u>. According to Berkeley observers (MP Berkeley 5) the melting point of US is considerably above 2000°C, that of U_2S_3, 1350°C ± 100°C and that of US_2, 1850°C ± 200°C.

<u>Magnetic Properties</u>. At Berkeley (MP Berkeley 6) the magnetic susceptibility of some uranium sulfide preparations was determined with the results listed in Table 46.

TABLE 46

MAGNETIC SUSCEPTIBILITY OF URANIUM SULFIDES

Compound	Molar Susceptibility (per g atom uranium)
US	4180×10^{-6}
U_2S_3	2630×10^{-6}
US_2	3050×10^{-6}

These results were taken as indicating that the U^{2+} ion in US has the configuration $5f^2$.

7.3 <u>Preparation of Uranium Sulfides</u>.

(a) <u>US</u>. Alibegoff (1886) prepared a product which he considered to be US by reduction of U_2S_3 with dry hydrogen at red heat. Flatt and Hess (1938) found that reduction of US_2 by hydrogen stops at U_2S_3 and therefore considered Alibegoff's conclusions as erroneous. At the Metallurgical Laboratory (MP Chicago 15) no reduction of US_2 by atomic hydrogen in quartz tubes was obtained at 200°C and 700°C.

At the Metallurgical Laboratory (MP Chicago 16) US was obtained by reduction of UOS with carbon at 1900°C in high vacuum:

(60) $UOS + C \longrightarrow US + CO$

One may expect that the equilibrium of the reaction:

(61) $UO + CS \rightleftharpoons US + CO$

also lies on the side of uranium sulfide formation.

According to Berkeley observers US can be prepared conveniently in the following two ways (MP Berkeley 5,7):

(1) The first method consists in interaction of fine uranium powder (obtained by decomposition of uranium hydride) with the calculated amount of hydrogen sulfide. The hydride is decomposed at 300°C and the residue is reacted with hydrogen sulfide at 400°C-500°C. The circulation of hydrogen sulfide is continued until the whole amount required has reacted. The product is at first not quite uniform but contains higher sulfides and unreacted metal; it can be heated to a higher temperature for homogenization. (US can be heated over 1800°C without decomposition.)

(2) The second method is the interaction of US_2 with the calculated amount of uranium hydride. The procedure is the same as above, decomposition of hydride at 300°C, heating to 400°C-600°C for the reduction of US_2 and final heating to high temperature for homogenization.

According to the same observers U_2S_3 can be decomposed to US by dissociation in high vacuum at 1800°C.

(b) $\underline{U_2S_3}$. Alibegoff (1886a) prepared U_2S_3 (greyish black needles) by heating UBr_3 in a hydrogen sulfide stream for eight-ten hours with complete exclusion of air. Flatt and Hess (1938) found that reduction of US_2 by oxygen-free hydrogen at red heat gives a greyish-black, pyrophoric powder whose analysis (83.2 per cent uranium) indicates the composition U_2S_3 (82.6 per cent uranium) rather than US (88.4 per cent uranium).

At Berkeley (MP Berkeley 5,8) three methods for the preparation of U_2S_3 were developed. The first two are identical with those described above for US:

(1) Reaction of uranium (from UH_3) with calculated amount of hydrogen sulfide; and

(2) Reaction of uranium (from UH_3) with calculated amount of US_2.

Because of instability of U_2S_3 at high temperatures the final homogenization of the product has to be carried out by prolonged heating at temperatures $\ll$ 1800°C.

(3) Thermal decomposition of US_2 (which can be obtained by reduction of uranium oxides with carbon in the presence of hydrogen sulfide, cf. below). In one experiment the decomposition of US_2 to U_2S_3 was complete after twenty minutes at 1600°C in a vacuum of about 10^{-4} mm Hg. However, since U_2S_3 is itself comparatively easily decomposed in vacuum (it can be converted to US in high vacuum at 1800°C), this method is less suitable than methods (1) and (2) for the preparation of a product with the composition corresponding exactly to the formula U_2S_3. On the other hand, the product obtained by this high temperature method consists of larger crystals and is much more stable in air than those obtained by the low temperature methods (1) and (2), the latter preparations having to be made and kept in an inert atmosphere.

(c) $\underline{US_{1.5<x<2}}$. At Berkeley (MP Berkeley 5,8) sulfides with compositions intermediate between $US_{1.5}$ (= U_2S_3) and US_2 were obtained by the three methods described under U_2S_3. Of these, thermal decomposition of US_2 is the easiest method if no exact final composition is desired.

(d) US_2. Péligot (1842d) discovered that uranium burns in boiling sulfur giving US_2. This is, however, not a convenient method of preparation of this compound. Another method is to react UCl_4 with hydrogen sulfide at red heat (Hermann, 1861):

$$UCl_4 + 2H_2S \longrightarrow US_2 + 4HCl \tag{62}$$

Colani (1903,1907) suggested the use of the less volatile $2NaCl \cdot UCl_4$ instead of UCl_4, and hydrogen charged with sulfur vapors instead of hydrogen sulfide (because hydrogen sulfide is difficult to dry). Air must be excluded. The reaction begins at 500°C. The product is washed with air-free water, alcohol and ether, and dried in vacuum. The disulfide can also be obtained by reaction of $2NaCl \cdot UCl_4$ with the sulfides of Na, Mg, Al, Sb and, even better, with tin sulfide at high temperatures but all these methods are not to be recommended. Traces of H_2O make the product impure.

At Ames (MP Ames 17) US_2 was prepared by action of hydrogen sulfide on UH_3 (or rather, on finely divided uranium obtained by dissociation of UH_3). Flatt and Hess (1938) prepared US_2 from U_3O_8 by first converting the oxide to UCl_4. After sublimation UCl_4 was converted to US_2 in the same tube by pure dry hydrogen sulfide. The product was a black mass.

At Berkeley (MP Berkeley 5,7) two methods were used: the above-mentioned Ames method involving UH_3 and the reduction of UO_2 or U_3O_8 with carbon in the presence of hydrogen sulfide. The latter reaction is fairly rapid at 1200°C-1300°C. UOS is the first product formed (cf. below, p. 148) but when the temperature is raised to its maximum value, UOS is reduced to US_2 by the action of CS (the latter being formed from hydrogen sulfide and C).

In order to prevent contamination of US_2 by lower sulfides, which may be caused by thermal decomposition of the disulfide at the temperatures used in the final stage of the preparation process, the temperature must be reduced to less than 1000°C, thus allowing the lower sulfides to pick up sulfur from the circulating hydrogen sulfide.

When pure uranium metal is available, the hydride method seems preferable because of its simplicity. However, in this case too, as in that of U_2S_3, the product obtained by the high temperature process is more stable than that obtained by the low-temperature hydride reaction.

7.4 Chemical Properties of Uranium Sulfides.

(a) US. Alibegoff (1886a) described uranium monosulfide as being hardly attacked by concentrated HCl and diluted HNO_3 and as slightly soluble in HCl + Br_2 solution. Fuming HNO_3 oxidized his material with ignition; aqua regia reacted less violently. However, this material might have been U_2S_3 rather than US (cf. p. 143). According to Berkeley observers US is very slowly soluble in dilute acids.

(b) U_2S_3. According to Alibegoff (1886a) and Flatt and Hess (1938) U_2S_3 decomposes in air and is often pyrophoric. In the presence of moisture it liberates hydrogen sulfide. Other U_2S_3 properties, according to Alibegoff, are similar to those described above under US. The same observer found that U_2S_3 can be reduced to US by heating in hydrogen to red heat. According to Berkeley observers (MP Berkeley 5) the decomposition pressure of U_2S_3 above 1800°C is high enough to make conversion to US possible also by heating in vacuum.

(c) $\underline{US_2}$. Hermann (1861) observed that US_2 oxidized in moist air very slowly evolving H_2S and leaving yellowish basic uranium sulfate. According to this author and also to Colani (1903, 1907) it is only very slowly attacked by water in the cold but is rapidly decomposed by water vapor. Dilute HCl has little effect; concentrated HCl attacks more rapidly, particularly on heating; HNO_3 acts very rapidly. Picon (1929) found US_2 to dissociate in vacuum at 1300°C evolving sulfur and forming a lower sulfide.

According to Ames observations (MP Ames 17) US_2 (made from uranium turnings via UH_3) reacted with bromine at 300°C liberating S_2Br_2. After heating to 600°C fused UBr_4 was obtained.

7.5 Uranium Oxysulfides.

Two uranium oxysulfides have been described in the earlier literature, $U_3O_2S_4$ (= $2UO_2 \cdot 2US_2$) and UO_3S (= $2UO_3 \cdot 2US_3$); the existence of the first one has been questioned by Berkeley observers. A third compound, UOS (= $UO_2 \cdot US_2$), was discovered at Berkeley.

(a) UOS. ($UO_2 \cdot US_2$) - Uranium(IV) - Oxysulfide. This compound was first obtained at Berkeley (MP Berkeley 7, 9) by reaction of UO_2 with (H_2S + H_2) at 1000°C-1200°C. The minute amount of water vapor produced by interaction of hydrogen sulfide with the oxide refractory suffices to inhibit the formation of US_2. Later it was found at Berkeley (MP Berkeley 5) that UOS can also be conveniently obtained by heating UO_2 or U_3O_8 with carbon in a stream of hydrogen sulfide; care must be taken to restrict temperature and duration of reduction so as to prevent formation of US_2.

The UOS is blue-black in color. Its structure was determined at Chicago (MP Chicago 2,17) as tetragonal with two molecules per unit cell (type PbFCl, isomorphous with ThOS), space group P_4/nmm:

2 U-atoms at $(00x_1)$ $(\frac{1}{2}\frac{1}{2}\bar{x}_1)$, with $x_1 = 0.200$
2 O-atoms at $(0\frac{1}{2}0)$ $(\frac{1}{2}00)$
2 S-atoms at $(00x_2)$ $(\frac{1}{2}\frac{1}{2}\bar{x}_2)$, with $x_2 = 0.65$

The lattice dimensions are

$$a_1 = 3.835 \pm 0.002A; \qquad a_3 = 6.682 \pm 0.002A.$$

The distances U-O are 2.34A; U-S, 2.93A. The calculated density is 9.60 g/cc.

UOS is soluble in concentrated nitric acid; it reacts with bromine water to give uranate and sulfate (MP Berkeley 5,9).

$\underline{UO_2 \cdot 2US_2}$ was discovered by Rose (1823) and first analyzed by Hermann (1861). It was described as dark lead-grey to black and was obtained by heating U_3O_8, UO_2 or ammonium uranate in carbon disulfide vapor. At Ames (MP Ames 16) the powder diagram of a product obtained from UO_2 and carbon disulfide was found to be different from those of UO_2 and US_2; the observed phase ($UO_2 \cdot 2US_2$?) was complex and its structure has not yet been determined.

The compound ignites in chlorine, is decomposed by fuming HNO_3 and slowly oxidized by chlorine water. It is easily decomposed by concentrated HCl (Hermann, 1861).

(b) UO_2S. (= $2UO_3 \cdot SO_3$), uranyl sulfide. This compound was first obtained by Berzelius (1824a) and then by Hermann (1861) by precipitating UO_2^{++} salts by $(NH_4)_2S$. The precipitate is gradually converted in the presence of air into the complex, highly colored products known as "uranium reds." (Cf. Part II, chapter on Uranates.) Pure, crystalline UO_2S was obtained by Milbauer (1904) from KCNS (twelve parts), UO_2 (three parts) and sulfur (five parts). The product forms black, tetragonal, needle-shaped crystals. It is converted to U_3O_8 by ignition in air with liberation of sulfur dioxide. Aqua regia or HNO_3 oxidizes it rapidly; HCl does not attack at room temperature but decomposes the uranyl sulfide on heating.

8. Uranium Selenides and Tellurides.

8.1 Selenides. Colani (1903,1907a) obtained uranium(IV) selenide, USe_2, by ignition at moderate red heat of $2NaCl \cdot UCl_4$ in hydrogen charged with selenium vapor. It also is formed by the action of SnSe on the sodium uranium(IV) double chloride in dry hydrogen stream. It forms small brittle, strongly reflecting black crystals and is often pyrophoric. Its chemical properties are similar to those of US_2 but it is more readily oxidizable, igniting on treatment with HNO_3. If too little selenium is used and the temperature is raised to 1000°C during preparation, U_2Se_3 is produced.

Uranyl selenide was obtained by Milbauer (1904a) by a method similar to the one he used for the preparation of UO_2S, namely, ignition of one part U_3O_8 with five parts KCN and seven parts selenium in a double crucible at bright red heat. The product was washed with water and alcohol and dried at 98°C. It forms small, metallic, lustrous, six-sided prisms which are black with a red tinge. Water decomposes it slowly, giving a red solution. It is not affected by dilute alkalis, is easily soluble in cold HCl (forming UO_2Cl_2) and reacts violently with HNO_3 forming at first selenium, which is then oxidized.

8.2 Tellurides. Colani (1903a,1907b) obtained a uranium telluride by heating 2NaCl·UCl_4 to 1000°C in a stream of dry hydrogen charged with Te vapor. The product had an approximate composition of UTe.

A second uranium telluride, U_2Te_3, was obtained by heating to 1000°C of 2 NaCl·UCl_4 with Na_2Te containing excess tellurium. It forms black, metallic-lustrous lamellae. The expected compound UTe_2 could not be obtained.

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P8

CHAPTER 12

THE NON-VOLATILE FLUORIDES OF URANIUM

CHAPTER 12

THE NON-VOLATILE FLUORIDES OF URANIUM

1. Uranium Trifluoride, UF_3

In contrast to uranium trichloride and tribromide, which are rather easily prepared and have been known for a long time, uranium trifluoride is a compound the preparation of which is attended with some difficulty; its synthesis has only recently been achieved. Early attempts to prepare UF_3 were made by reduction of the tetrafluoride with hydrogen at elevated temperatures, a method which was successfully used earlier for the preparation of UBr_3 and UCl_3. In the first such attempt (Bolton, 1866) the tetrafluoride used was prepared from aqueous solution and, therefore, probably contained small amounts of water. When this material was treated with dry hydrogen at red heat, hydrogen fluoride was evolved and a reddish-brown mass was obtained. It was insoluble in water and was scarcely attacked by any acid with the exception of concentrated nitric acid. No analysis of the production was made, but Bolton surmised that it was a lower fluoride. However, recent work has shown that in the presence of traces of oxygen or water, reaction of uranium tetrafluoride with hydrogen leads to uranium dioxide rather than to the tribromide. Thus, Gates and Andrews (CEW-TEC 1), who treated uranium tetrafluoride with hydrogen at 450°-550°C, obtained as product only impure UO_2, probably because of the presence of oxygen in the tank hydrogen used. British investigators (British 1) also tried to obtain UF_3 by treating uranium tetrafluoride with hydrogen at 600°. They, too, observed an evolution of hydrogen fluoride but failed to identify the product as UF_3.

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The presumption that uranium trifluoride might be of use for the production of uranium metal led the Ames group to devote considerable attention to the preparation of this compound (MP Ames 1,2). First, the reaction of hydrogen with UF_4 was re-investigated. The hydrogen was rigorously purified by passage over hot uranium metal (Chapter VI, Section 1.1). It was found that if the reaction was carried out in a silica reaction tube, fluorine-containing gases were evolved at temperatures above 600°C. The product, however, was largely UO_2. The following explanation was given for this result: In the presence of traces of moisture, a small amount of tetrafluoride undergoes hydrolysis with the production of hydrogen fluoride and UO_2; the latter attacks the silica, giving SiF_4 and more water; the cycle is repeated until complete conversion of the UF_4 to UO_2 results. This is particularly likely to occur when the hydrogen flow through the system is slow. When the reaction of UF_4 with hydrogen was carried out in a monel reaction tube, no evolution of hydrogen fluoride was observed at all. Even after forty-eight hours treatment with pure hydrogen at 980°C the UF_4 could be recovered substantially unchanged. This result of the Ames investigations is not quite understandable since we will see below that British investigators succeeded in preparing UF_3 by substantially the same method. The Ames group, however, abandonded hydrogen reduction and turned their attention to other preparative methods.

A number of unsuccessful attempts were made in various laboratories to prepare UF_3 by halogen exchange reactions with UH_3, UCl_3, or UBr_3. Whereas UBr_3 and UCl_3 are formed easily when UH_3 is treated with hydrogen bromide or chloride, the action of hydrogen fluoride on UH_3 yields only UF_4 (MP Ames 3):

(1) $UH_3 + 4HF \xrightarrow{400^\circ C} UF_4 + 7/2\ H_2$

Andrews and Gates (CEW-TEC 1) treated UCl_3 with anhydrous hydrogen fluoride at 450°C and also obtained UF_4:

(2) $UCl_3 + 4HF \rightarrow UF_4 + 3HCl + 1/2\ H_2$

The Brown University Group (Brown 1) treated anhydrous uranium trichloride with liquid anhydrous hydrogen fluoride at 25°C and observed the evolution of hydrogen chloride. No details of the experiment were given, but the statement was made that the product obtained oxidized rapidly in dry air and that presumably it was the trifluoride. However, the easy oxidation of the product does not agree well with the known stability of the trifluoride, and the reaction therefore requires further study.

An earlier observation made by the same group (Brown 2) indicated that a reddish, rapidly oxidizing precipitate also is formed by the addition of aqueous hydrofluoric acid to an aqueous solution of uranium trichloride. This observation was confirmed at Ames and at the UCRL. (MP Ames 4; UCRL 1). However, only uranium tetrafluoride could be isolated from the product, despite the transitory appearance of a reddish-brown color in the precipitate. Since it appeared reasonable that rapid reaction of UF_3 with water might be responsible for the failure, the experiments were repeated in a non-aqueous solvent (MP Ames 5). A solution of UBr_3 in diethylformamide was treated with anhydrous hydrogen fluoride. (Previous experiments had shown diethylformamide to be unaffected by hydrogen fluoride.) However, instead of the expected red precipitate of UF_3, only a green tarry paste resulted which must have been formed by reaction with the solvent. Thus, uranium trifluoride could not be prepared by any of these halogen exchange reactions.

1.1 Preparation of Uranium Trifluoride. Two successful preparations of uranium trifluoride have thus far been achieved. In the first, by a careful attention to the effects of moisture, oxygen and to the purity of the uranium tetrafluoride, British workers succeeded in preparing the trifluoride by reduction of the tetrafluoride with hydrogen (British 2). In the second preparation the Ames group obtained UF_3 by the reduction of the tetrafluoride with metallic uranium.

(a) Reduction of UF_4 with Hydrogen (British 2). The success of this procedure is contingent upon the exclusion of all traces of moisture or oxygen. The hydrogen is rigorously purified: After preliminary drying over calcium chloride, oxygen is removed by palladium-asbestos at 350°C, and final drying is achieved by successive passage through calcium chloride, phosphorus pentoxide, and a trap cooled by liquid nitrogen. Traces of suspended solid impurities are removed from the gas stream by a sintered glass filter.

The reaction tube consists of an outer tube of silica fitted with a liner of stainless steel (18/8/1/1) to prevent the hydrogen fluoride produced in the reaction from attacking the silica tube. In large scale preparations a stainless steel tube alone is sufficient. A molybdenum boat can be used for holding the tetrafluoride. All exposed silica surfaces in the cooler parts of the apparatus are protected by a coating of ceresine wax. The entire apparatus is evacuated, thoroughly dried, and degassed before use.

To obtain pure uranium trifluoride it is essential to use tetrafluoride which is free of oxygen-containing impurities. Uranium tetrafluoride prepared from aqueous solution, and containing as chief impurities tin, copper, sulfate, and water, gives mixtures of UF_3 and UO_2 since at the high temperatures used, both sulfate and water react with UF_4. Even uranium tetrafluoride prepared from UO_2 by high temperature hydrofluorination, a material which is ordinarily considered as anhydrous, contains enough moisture to cause contamination of the product with UO_2. It has been found that UF_4 of sufficient purity can be prepared by sublimation of ordinary UF_4 in a very good vacuum at 1000°C using a molybdenum apparatus. Very pure crystalline material suitable for conversion to UF_3 can be obtained in this way.

The reduction of UF_4 by hydrogen proceeds quite rapidly at 1000°C (above the melting point of UF_4) according to the equation:

$$(3) \quad 2UF_4 + H_2 \rightleftharpoons 2UF_3 + 2HF$$

Below 900°C reduction is negligible. Reduction beyond the trifluoride state is very slow at 1000°C. Prolonged heating at 1000°C is inadvisable as there is danger of thermal disproportionation of the trifluoride (See Sec. b below). The product obtained by reduction of UF_4 with hydrogen is crystalline and has a deep violet-red color. That it is pure UF_3 is shown by chemical analysis and by x-ray crystallography.

Uranium trifluoride has also been prepared, although on a very small scale, by the action of atomic hydrogen on UF_4 in a silica vessel (MP Chicago 1). A product was obtained the x-ray diffraction pattern of which indicated the presence of 60 per cent UF_3 and 40 per cent UO_2. The oxygen probably arises from water formed by the reaction of atomic hydrogen with silica.

(b) Reduction of UF_4 by Uranium Metal (M P Ames 6). Uranium tetrafluoride can be reduced with finely divided uranium at 1050°C:

(4) $3UF_4 + U \rightleftharpoons 4UF_3$

Temperature regulation is important since reaction (4) is reversible, and above 1050°C the equilibrium is markedly displaced to the left. The reaction may be carried out in a nickel vessel by mixing uranium tetrafluoride with the stoichiometric amount of uranium turnings. The mixture is heated to 250°C, and hydrogen introduced to convert the metal to hydride. The hydride is then decomposed at 400°C, giving an intimate mixture of UF_4 with finely divided uranium metal. This mixture is fused at 1050°C for two hours in an argon atmosphere and a black, dense, coke-like solid is obtained. Analysis indicates that it is substantially pure UF_3 contaminated with about one per cent of UO_2 and UO_2F_2.

1.2 Physical Properties of Uranium Trifluoride. Uranium trifluoride obtained by the reduction of uranium tetrafluoride with hydrogen is a fused crystalline mass almost black in the massive form. Under the microscope the crystals appear violet-red in color. Since the trifluoride disproportionates (to UF_4 and U) above 1000°C, the melting point could not be determined, but observations indicate that it must lie above 1140°C. The compound appears to be very slightly volatile above 1000°C (M P Ames; 6; British 2).

X-ray diffraction studies (M P Chicago 2; M P Ames 7) showed that uranium trifluoride has a crystal structure very different from that of the tetrafluoride; it is isomorphous with the rare earth fluorides, LaF_3, PrF_3, CeF_3, and NdF_3 .

The X-ray powder diagram is characteristic of an hexagonal, close packed arrangement of the metal atoms. The unit cell contains two molecules (space group $C6/mmc$). The parameters, as determined by Zachariasen

TABLE 1

X-RAY DATA ON UF_3 AND SOME ISOMORPHOUS COMPOUNDS

Substance	Lattice Dimensions A (a)		Density	Interatomic Distances (b)			Ionic (c) Radius A
	a_1	a_3		3F at	2F at	6F at	M (III)
LaF_3	4.140 ±.001	7.336 ±.001	...	2.39	2.38	2.71	1.06
UF_3	4.138 ±.003	7.333 ±.004	8.95 (d)	2.39	2.38	2.71	1.06
CeF_3	4.107 ±.003	7.273 ±.005	...	2.37	2.36	2.69	1.04
PrF_3	4.077 ±.003	7.218 ±.007	...	2.35	2.35	2.67	1.03
NdF_3	4.054 ±.003	7.196 ±.005	...	2.34	2.34	2.66	1.01

a. Assuming hexagonal structure.

b. There are eleven fluorine atoms about each metal atom.

c. After correction to coordination number eight and subtraction of the ionic radius for F^- (1.33 A°).

d. British workers have found a density of 9.18 g/cm^3 by immersion in tetralin.

(M P Chicago 2) on a very pure sample of LaF_3 are given in Table 1 together with those of UF_3 from Zachariasen and those of CeF_3, PrF_3 and NdF_3 from Oftedal (1929, 1931). However, I. Oftedal stated that the true unit cell, as determined by Laue photographs, is orthorhombic, and is three times larger than the hexagonal unit cell deduced from powder diffraction patterns. In agreement with this view, British workers (British 3) found by goniometric measurements that the crystals of UF_3 are probably orthorhombic. The crystals are weakly birefringent with all of the refractive indices close to 1.73. All the crystals seem to exist as triplets, twinned on a submicroscopic scale.

1.3 Chemical Properties of Uranium Trifluoride. (a) Thermal Disproportionation. British workers (British 2) found that uranium trifluoride decomposes above 1000°C:

(5) $4UF_3 \rightleftharpoons 3UF_4 + U$ (See equation 4)

In vacuum, UF_4 sublimes and uranium metal powder is left. The decomposition is slight at 1000°C and becomes considerable at 1200°C. The failure of the Ames Group to obtain UF_3 by the reaction of U and UF_4 at 1400°C is in agreement with these results. It has been proposed to utilize the disproportionation of UF_3 for the preparation of very pure uranium metal, but the difficulty of finding materials which would resist the action of both metal and fluoride at such high temperatures render success improbable.

(b) Effect of Air Uranium trifluoride is only slowly affected by moist air at room temperature (British 2). It is not appreciably hygroscopic thereby resembling the trichloride in stability. On heating in air, oxidation occurs, presumably to an oxyfluoride. At 900°C uranium trifluoride is quantitatively converted in air to U_3O_8 .

(c) Water. Uranium trifluoride is insoluble in water. In cold water it is slowly oxidized to a green gelatinous material; at 100°C attack is much more rapid, and the supernatant solution acquires the yellow color indicative of oxidation to the hexavalent state (British 2).

(d) Acids. (British 2; M P Ames 6). Similar to the rare earth fluorides UF_3 is rather inert to acids. Like the rare earth fluorides (and in contradistinction to UF_4) UF_3 is insoluble in ammonium oxalate. Acids with oxidizing power convert UF_3 to uranyl salts and thus dissolve it. Dilute hydrochloric, sulfuric and nitric acids attack UF_3 only slowly in the cold. Hot nitric acid dissolves UF_3 fairly rapidly with the evolution of nitrogen oxides. Hot dilute sulfuric acid also dissolves UF_3 but rather more slowly than nitric acid. Hot perchloric acid yields clear solutions of uranyl perchlorate, $UO_2(ClO_4)_2$. Ames investigators thought that the reaction of UF_3 with hydrochloric acid is an oxidation,

(6) $4UF_3 + 4HCl \longrightarrow \underline{3UF_4} + UCl_4 + 2H_2$,

but British workers stated that with either dilute or concentrated hydrochloric acid deep red solutions are obtained, a color indicative of the presence of U(III) ions. This observation is in agreement with the known stabilizing effect of hydrochloric acid on U(III) solutions. The addition of boric acid to hydrochloric acid or other acids results in the formation of fluoborate complexes which markedly facilitate dissolution.

(e) Oxidizing Agents. (M P Ames 6; British 2). Cupric chloride-ammonium chloride mixture, which dissolves uranium metal readily, attacks UF_3 only slightly. Ferric nitrate dissolves UF_3. Silver perchlorate solution is reduced rapidly, giving a silver mirror. Chlorine reacts to give UF_3Cl (cf. Chapter XIV, Section 4) (M P Ames 8). The effect of fluorine has not been investigated; doubtless UF_6 would be the ultimate product although interesting intermediates might be encountered.

(f) Reducing Agents (M P Ames 9). Uranium trifluoride has been successfully reduced to metal with calcium by the usual Ames uranium preparation technique. An iodine booster charge was added (0.5 mole I_2/mole UF_3), together with a 30 per cent excess of calcium. Yields of well-formed massive metal as high as 98 per cent have been obtained in this way.

2. URANIUM TETRAFLUORIDE

Uranium tetrafluoride, long and obscure compound, has in recent years achieved considerable importance. Much effort has been expended in studying its preparation and chemical properties. Two types of preparative methods are now available. The first is based on the precipitation of UF_4, which is practically insoluble in water, from aqueous solutions of other U(IV) compounds:

(7) $U^{+4}_{aq} + 4F^{-}_{aq} \longrightarrow \underline{UF_4}$

The second method involves the reaction of various uranium compounds, particularly uranium dioxide, with gaseous fluorinating agents at elevated temperatures, for example:

(8) $UO_2 + 4HF \xrightarrow{550°C} UF_4 + 2H_2O$

This method is distinguished by simplicity of procedure and the relative ease with which a pure, anhydrous product can be obtained.

In the following reaction, a description of the various methods of preparation of UF_4 will be given. Emphasis will be placed on the chemical principles rather than on the details of the actual procedures.

2.1 Early Work. Uranium tetrafluoride was first prepared by the action of aqueous hydrofluoric acid on U_3O_8 (Hermann, 1861). The reaction is vigorous and yields a yellow solution together with a green insoluble residue. The composition of this residue was correctly determined as UF_4 by Bolton (1866):

(9) $U_3O_8 + 8HF \longrightarrow 2UO_2F_2 + \underline{UF_4} + 4H_2O$

Uranium tetrafluoride prepared in this way is very difficult to filter and wash. Bolton obtained a more easily filterable product by the reduction of a boiling solution of uranyl fluoride, UO_2F_2, with stannous chloride and with periodic addition of hydrofluoric acid. Solutions of ammonium uranate or ammonium uranyl carbonate in hydrofluoric acid also yielded an easily purifiable uranium tetrafluoride when reduced in the same way. Bolton also observed that addition of hydrofluoric acid to a solution of uranium tetrachloride produced a voluminous precipitate of uranium tetrafluoride. Both Hermann and Bolton reported that ignited uranium dioxide reacted very slowly with aqueous hydrofluoric acid; freshly precipitated $UO_2 \cdot xH_2O$ reacted much more rapidly. This observation finds confirmation in the work of Braddock and Copenhafer (Mallinckrodt 1) who noted that hot, constant-boiling hydrofluoric acid (43.2 per cent HF) gave no uranium tetrafluoride with anhydrous uranium dioxide even after considerable period of time. Conversion of UO_2 to UF_4 is apparently accelerated by dilution of the hydrofluoric acid. Ditte (1880) also studied the action of hydrofluoric acid on U_3O_8 with results which he claimed were not in agreement with those of Bolton. Ditte's results are, however, valueless because of poor analytical technique, and a repetition of the experiments by Smithells (1883) confirmed Bolton's original conclusions.

2.2 Preparation of Uranium Tetrafluoride in Aqueous Solutions. Wet methods for the preparation of UF_4 have been developed mostly by British workers. Their various modifications are all based on the above-mentioned early work of Bolton. Essentially, they consist in reducing solutions of uranyl fluoride, chloride, or sulfate to the tetravalent state and precipitating uranium tetrafluoride by the addition of hydrofluoric acid. Various uranium compounds have been employed as starting materials, and a variety of reducing agents have been suggested.

(a) Stannous Chloride-Hydrofluoric Acid Processes. Grosse (S A M-Columbia 1) prepared UF_4 in much the same fashion as did Bolton by dissolving sodium uranate, Na_2UO_4, in excess hydrofluoric acid, and reducing the solution with stannous chloride at the boiling temperature. A yield of 99 per cent was reported by him.

(10) $Na_2UO_4 + 4HF \longrightarrow UO_2F_2 + 2NaF + 2H_2O$

(11) $UO_2F_2 + SnCl_2 + 4HF \longrightarrow \underline{UF_4} + SnCl_2F_2 + 2H_2O$

A repetition of this work (British 4,5) showed, however, that the uranium tetrafluoride so obtained was invariably contaminated with sodium fluoride (4-5 per cent after drying at 100°C). The amount of sodium fluoride did not correspond to any definite compound of NaF and UF_4; probably, the precipitate was a mixture of UF_4 with some double salt of UF_4 and NaF, the exact ratio of the two components being dependent on the relative solubilities of the double salt and of UF_4 in aqueous hydrofluoric acid. Since sodium fluoride is an undesirable contaminent efforts were made to prepare sodium-free UF_4. It was found that this result can be achieved by using sodium uranate (or probably the more easily available diuranate, $Na_2U_2O_7$) in hydrochloric or sulfuric acid (rather than hydrofluoric acid) solution.

British investigators (British 5, 6, 7) found, for example, that UF_4 containing less than 0.1 per cent sodium can be obtained by first dissolving $Na_2U_2O_7$ in excess hydrochloric acid:

(12) $Na_2U_2O_7 + 6HCl \longrightarrow 2UO_2Cl_2 + 2NaCl + 3\ H_2O$

(13) $UO_2Cl_2 + SnCl_2 + 4HCl \longrightarrow UCl_4 + SnCl_4 + 2H_2O$

(14) $UCl_4 + 4HF \longrightarrow \underline{UF_4} + 4HCl$

In order to obtain an easily filterable UF_4 precipitate, very efficient stirring and vigorous boiling are required. The hydrogen fluoride must be added slowly and in large excess (100 per cent).

The kinetics of the reduction of uranyl ions by stannous ions Sn (II) has been investigated (British 4); the results are consistent with slow, ionic reaction. The rate increases rapidly with temperature between 17°C and 110°C. For rapid reduction, therefore, the solution must be as hot as possible. The presence of excess hydrochloric acid also tends to increase the rate of reduction. Fairly good yields (92-97 per cent UF_4) can be obtained by this procedure, but the corrosion problems encountered in handling hot solutions containing both hydrochloric and hydrofluoric acids are very troublesome. Ebonite affords a partial solution of the difficulty since it is resistant to solutions of 10 per cent hydrochloric acid and 5 per cent hydrofluoric acid (British 8), but ebonite vessels can not be heated to a high enough temperature. This process was therefore modified (British 9,10) by using sulfuric acid instead of hydrochloric acid. This permits the employment of lead-lined vessels.

(15) $Na_2U_2O_7 + 3H_2SO_4 \longrightarrow 2UO_2SO_4 + 3H_2O + Na_2SO_4$

(16) $2UO_2\ SO_4 + 2SnCl_2 + 4H_2SO_4 \longrightarrow 2U(SO_4)_2 + 2SnCl_2 \cdot SO_4 + 4H_2O$

A complication is introduced by the fact that sparingly soluble $U(SO_4)_2 \cdot 4H_2O$ may precipitate and contaminate the tetrafluoride (See section d).

Sodium diuranate proved not to be the most suitable starting material for the preparation of UF_4, and the tin chloride reduction method was modified so that U_3O_8, which is more readily available, could be used instead of the diuranate. A preliminary investigation of the dissolution of U_3O_8 by various acids showed that solutions of uranyl chloride or sulfate could be obtained by reaction of U_3O_8 with the appropriate acid in the presence of an oxidizing agent such as HNO_3 (British 11,12):

(17) $U_3O_8 + 6HCl + 2HNO_3 \longrightarrow 3\,UO_2Cl_2 + 4H_2O + 2NO_2$

By using somewhat less than stoichiometric quantities (85 per cent) of nitric acid, it is possible to obtain solutions free of excess nitric acid. Since, as mentioned above, hydrochloric acid gives rise to corrosion difficulties, here too, its use, despite some desirable features, was also abandoned in favor of sulfuric acid (British 13).

U_3O_8 dissolves very readily in mixtures of sulfuric and nitric acids, especially at moderately elevated temperatures. If the quantities of acids used are exactly stoichiometric according to the equation,

(18) $2U_3O_8 + 6H_2SO_4 + 2HNO_3 \longrightarrow 6UO_2SO_4 + NO_2 + NO + 7H_2O$

a smooth and rapid conversion of U_3O_8 to UO_2SO_4 can be obtained (British 14). Once a solution of UO_2SO_4 is available, the reduction can be performed exactly as in the procedures described before (British 15), and UF_4 precipitated as described in detail in section (d).

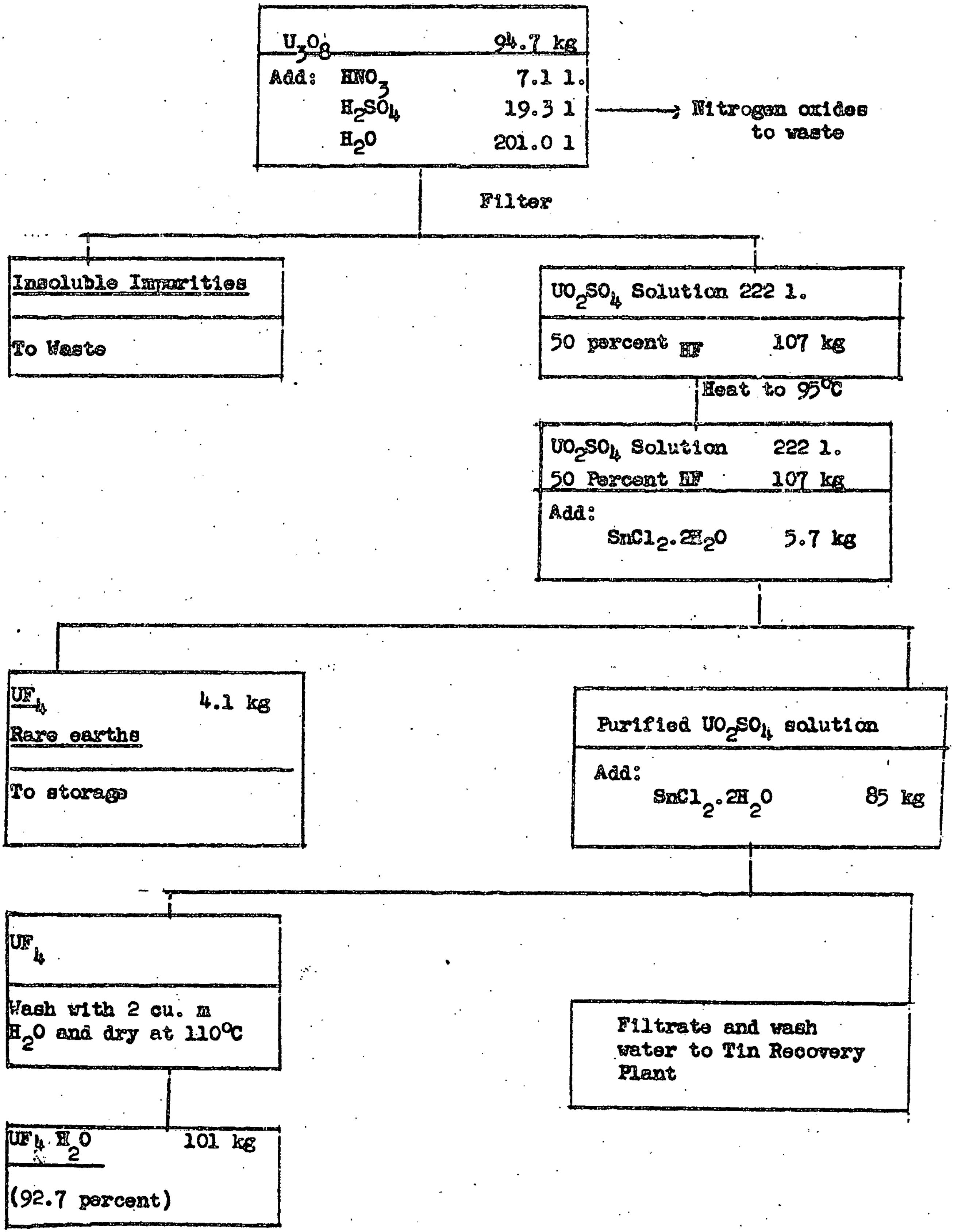
(b) <u>Preparation of UF_4 Free fr m Rare Earths by the $SnCl_2$-HF Process</u> (British 16). For certain purposes the rare earths constitute a most serious impurity in commercial U_3O_8. The rare earth content of the tetrafluoride can be reduced very substantially by the following procedure:

U_3O_8 is dissolved in HNO_3-H_2SO_4 mixture to give UO_2SO_4 solution. Eight moles of hydrofluoric acid per mole of uranium are added to the uranyl sulfate solution which is then heated to boiling. Addition of hydrofluoric acid at this point is permissible since there is no danger here of NaF co-precipitation. The boiling solution is then reduced by the slow addition of solid stannous chloride. The first portion of precipitate formed is removed; it contains practically all of the rare earths. The remainder of the UF_4 is then precipitated in the same way (Fig. 1). The product obtained according to the flow sheet is a monohydrate, $UF_4 \cdot H_2O$, and contains approximately 0.3 per cent tin and variable amounts of sulfate. The dehydration of the monohydrate is difficult, and this aspect of the problem of producing UF_4 from aqueous solution has not been solved satisfactorily. On the whole this method of preparing UF_4 is useful only if a product containing some tin, sulfate, and moisture can be utilized. This method is also useful when only impure U_3O_8 is available and it is necessary to prepare uranium tetrafluoride free of rare earths.

Zinc metal may be used instead of $SnCl_2$. Although the formation of U(III) is likely to be troublesome, this can be minimized by careful reoxidation to U(IV) with air.

(c) Preparation of UF_4 by Electroytic Reduction of Uranyl Compounds. Uranyl sulfate solutions can also be reduced to U(IV) sulfate electrolytically, and UF_4 can then be precipitated by the addition of hydrofluoric acid. This procedure dispenses with the use of stannous salts and yields a purer product since no contamination with a chemical reducing agent can occur. However, no convenient method is known for removing rare earths in this process (British 16). Therefore, if a rare-earth-free product is

THE PREPARATION OF $UF_4 \cdot H_2O$ FREE OF RARE EARTHS



desired, the appropriate starting materials for the electrolytic process are uranium oxides obtained from uranyl nitrate which has been previously subjected to solvent extraction, and which is consequently free of rare earths.

Uranium dioxide was used as material in this work; like U_3O_8 (See equation 18), it dissolves readily in a mixture of nitric and sulfuric acids:

(19) $3\,UO_2 + 3H_2SO_4 + 2HNO_3 \rightarrow 3UO_2SO_4 + 4H_2O + 2NO$

(20) $2UO_2 + 2H_2SO_4 + 2HNO_3 \rightarrow 2UO_2SO_4 + 3H_2O + NO + NO_2$

Both reactions occur simultaneously. Reaction (19) is the principal one, but the importance of reaction (20) increases with rising temperature; it is also enhanced by the presence of excess oxidizing agent. If 1 kg. of UO_2 is added to 2.13 kg of mixed acid (H_2SO_4, 17.96 per cent; HNO_3 7.95 per cent; H_2O, 74.09 per cent) at 50°-70°C, moderate effervescence occurs, and after heating for three hours at 100°C, more than 97 percent of the UO_2 will be in solution as uranyl sulfate. The solution obtained in this way contains very little free nitric acid and is suitable for conversion to $U(SO_4)_2$ by electrolytic reduction (British 17). The dissolution of uranium dioxide in acid can be very violent; the conditions and concentrations specified above have been found to ensure smooth reaction.

Electrolytic reduction is performed in lead-lined cells fitted with platinum electrodes and equipped with porous-pot diaphragms (British 18). The reduction is carried out at about 55°C. The concentration of uranium is usually around 125 g/liter; knowledge of the initial concentration is important and this can be easily determined by density measurements (British 19). As the reduction proceeds, the current efficiency falls due to the change in ratio of U(IV)/U(VI). The current is therefore progressively decreased and the electrolysis is stopped at 95 per cent reduction. The course of the reduction is readily followed by titration with potassium permanganate.

(d) <u>Precipitation of UF_4 from U(IV) Sulfate Solutions</u> (British 20). To produce a fast-settling precipitate of UF_4 from the $U(SO_4)_2$ solution, the reaction must be carried out at the boiling point. Heating of a $U(SO_4)_2$ solution to this temperature creates, however, the danger of precipitation of $U(SO_4)_2 \cdot 4H_2O$. To prevent this one half of the four moles of hydrofluoric acid required for complete precipitation of UF_4 is added to the cold solution (thus forming a soluble complex, see below). The solution is then brought to the boiling point, and a 30 per cent excess of hydrofluoric acid is added slowly while the solution is maintained at the boiling point. Stirring is essential but should not be continued after precipitation has been completed. The precipitate settles rapidly enough to permit washing by decantation. Experience has shown that soluble impurities not removed after three washes are permanently absorbed or occluded, and cannot be eliminated by repeated washings (British 21). As a result of occlusion, uranium tetrafluoride prepared in this way always contains some sulfate.

$U(SO_4)_2 \cdot 4H_2O$ is the solid phase in equilibrium with a U(IV) sulfate solution above 70°C, and it is so slightly soluble that a precipitate forms whenever a U(IV) sulfate solution containing more than 5g/100cc is heated to this temperature. It was found, however, that $U(SO_4)_2 \cdot 4H_2O$ dissolves in aqueous hydrofluoric acid. Milky suspensions of $U(SO_4)_2 \cdot 4H_2O$ can also be dissolved by the addition of HF or even of suspensions of sodium fluoride. That dissolution is caused by the formation of a sulfate-fluoride complex, is confirmed by the observation that more than two moles of hydrofluoric acid must be added per mole of U(IV) sulfate in solution before any precipitation of UF_4 occurs (British 23). When a solution of $U(SO_4)_2$ is treated with less than two moles of hydrofluoric acid, it merely changes color (British 24).

All of these observations indicate that the precipitation of UF_4 is preceded by the formation of a soluble complex:

(21) $U(SO_4)_2 + 2HF \longrightarrow$ soluble complex

(22) Soluble complex $+ 2HF \longrightarrow \underline{UF_4}$

As indicated in equation (21), the complex probably contains $U(SO_4)_2$ and HF in the ratio of 1:2. The brutto formula thus must be $U(SO_4)_2 \cdot 2HF$; by analogy with other quadrivalent uranium compounds, in which uranium is known to have a co-ordination number of six, the structural formula probably is $H_2[U(SO_4)_2F_2]$. If the complex does have this constitution, it is an acid, and it should be possible to prepare its salts. A compound $K_2[U(SO_4)_2F_2] \cdot 2H_2O$ has in fact been prepared from $U(SO_4)_2$ and KF.

The stability of the complex $H_2[U(SO_4)_2F_2]$ has been studied in some detail. Its solutions give qualitative test for U(IV) (e. g., precipitation of $U[Fe(CN)_6]$). Therefore, the complex must be markedly dissociated into UF_4 and $U(SO_4)_2$. Including the ionic dissociations of the complex, HF and of $U(SO_4)_2$, the following equilibra must therefore exist in the solution containing two moles HF per mole $U(SO_4)_2$:

$$\begin{array}{llcl}
(23) & U(SO_4)_2 + 2HF & \rightleftharpoons & H_2[U(SO_4)_2F_2] \\
 & \quad\quad\quad \updownarrow & & \quad\quad \updownarrow \\
(24) & U^{+4} + 2SO_4^{-} + 2H^+ + 2F^- & \rightleftharpoons & 2H^+ + [U(SO_4)_2F_2]^{=}
\end{array}$$

When such a solution is allowed to stand (at any temperature between

20° and 100°C) a slow precipitation of UF_4 occurs. Careful study showed that this is not caused by partial oxidation of U(IV) to U(VI) by air, but is probably due to slow decomposition of the complex:

$$(25)\quad 2H_2\left[U(SO_4)_2F_2\right] \rightarrow UF_4 + U(SO_4)_2 + 2H_2SO$$

At 20°C only UF_4 precipitates after about 48 hours, probably as $2UF_4 \cdot 5H_2O$. The $U(SO_4)_2$ formed according to equation (25) remains in solution, since the octahydrate $U(SO_4)_2 \cdot 8H_2O$, which is the stable solid phase at temperatures up to 70-80°C is highly soluble. At 100°C precipitation of UF_4 commences in one-half hour. At this temperature, the monohydrate, $UF_4 \cdot H_2O$ is the form precipitated. When the solubility limit of $U(SO_4)_2 \cdot 4H_2O$ is reached, $UF_4 \cdot H_2O$ and $U(SO_4)_2 \cdot 4H_2O$ precipitates as mixed crystals.

It was observed (CEW TEC 2) that UF_4 suspensions, which have been fumed with sulfuric acid for a short time, dissolve when the acid is diluted with water. This can be interpreted as additional evidence for the formation of the complex $H_2\left[U(SO_4)_2F_2\right]$.

(e) Precipitation and Dehydration of $2UF_4 \cdot 5H_2O$. (SAM Columbia 2). UF_4, precipitated at room temperature, is an amorphous green mass which is extremely difficult to filter and wash. To obtain a crystalline, easily filterable uranium tetrafluoride, the following procedure has been found useful. The amorphous precipitate is suspended in dilute hydrofluoric acid (0.1 to 3 per cent) for a period ranging from a few hours to a few days. This converts it into a voluminous, sometimes gelatinous, mass of long thin, silky, turquoise-colored needles. When the conversion is complete, the crystals can easily be filtered and washed. The air-dried crystals have a constant composition and do not lose weight in vacuum at room temperature. Analysis indicates the formula to be $2UF_4.5H_2O$. This hydrate is said to be very stable in air, with practically no oxidation to hexavalent uranium even after standing several weeks.

(g) Preparation of Anhydrous Uranium Fluoride from the Hydrates. Moist uranium tetrafluoride can be dried in air at 100°C to give a hydrated uranium tetrafluoride approximating the monohydrate, $UF_4.H_2O$, in composition. In air at 400°C the water of hydration is removed, but there is considerable hydrolysis and oxidation (British 25). Drying in a stream of inert gas (nitrogen) at 400°C has been tried but abandoned because of the difficulty in eliminating oxygen, traces of which suffice to cause oxidation. Dehydration of the monohydrate at a temperature of 400°C and a pressure less than 50 mm Hg yields fairly satisfactory results. The period of heating should be as brief as possible and the surface area of exposed monohydrate should be as small as possible to minimize surface oxidation. A product containing about 0.20 per cent water and an oxygen content equivalent to 3 per cent UO_2F_2 can be obtained in this way.

It has been found that satisfactory dehydration of $UF_4.H_2O$ can also be achieved by heating in a stream of hydrogen fluoride under atmospheric pressure. Even more satisfactory is dehydration at reduced pressure (50mm) in the presence of a small proportion of hydrogen fluoride (5 mm) at 400°C. Under these conditions practically no oxycompounds are formed; the presence of even small amounts of hydrogen fluoride retards their formation to a very marked degree (British 26).

Uranium tetrafluoride 2.5 hydrate, $2UF_4.5H_2O$, is reported to lose most of its water readily without side reaction during slow heating at 200°C in vacuum (2 mm Hg pressure) for twenty-four hours. The last traces, however, are eliminated only at 500°-550°C (SAM-Columbia 2). Occasionally traces of hydrogen fluoride are found in the exit gases during dehydration. It is advisable to employ as good a vacuum as possible and to increase the temperature gradually. According to a more recent study, $UF_4.2.5H_2O$ is best dehydrated by heating in anhydrous hydrogen fluoride at 450°C (Sam-Columbia 3). The anhydrous product retains the voluminous appearance of the hydrate and therefore has a low bulk density (1.5 g/cc). It re-hydrates much more readily than UF_4 prepared by high temperature hydrofluorination. The large surface area (6-8 m^2/g) of the dehydrated material makes it especially suitable for heterogeneous reactions (i.e., preparation of UF_6, UF_5, U_2F_9, etc).

The desirability of having HF present in the atmosphere in which UF_4 is being dried will be justified in Section 2.6 by showing the relative ease with which UF_4 can be hydrolysed according to its thermodynamic properties.

2.3 <u>Preparation of Uranium Tetrafluoride by Vapor Phase Reactions at Elevated Temperatures.</u> For certain purposes uranium tetrafluoride as completely free of water and oxycompounds as possible is required. When prepared from aqueous solution, uranium tetrafluoride almost invariably contains small amounts of water, and often considerable amounts of oxycompounds which arise either from oxidation or from hydrolysis during dehydration. Other contaminants such as tin, zinc, or sulfur-containing compounds (e.g. sulfate) may also be present.

The methods now to be described are better adapted to the preparation of an oxygen-free anhydrous product. They consist of the treatment of uranium compounds, usually oxide, with gaseous fluorinating agents, usually anhydrous hydrogen fluoride.

(a) Preparation of UF_4 by Hydrofluorination of UO_2. The preferred sequence of operations* is: hydrogen reduction of UO_3 followed by treatment of the resulting UO_2 with anhydrous hydrogen fluoride at atmospheric pressure.

(26) $UO_3 + H_2 \longrightarrow UO_2 + H_2O$

(27) $UO_2 + 4HF \longrightarrow UF_4 + 2H_2O$**

The reduction of UO_3 is carried out at 600°-700°C. Since the state of the UO_2 has an important bearing on the rate of the next reaction step, much attention has been devoted to obtaining an "active" UO_2. The lower the temperature at which the reduction is carried out, the more reactive the dioxide will be in the hydrofluorination step. The importance of the particle size of the original UO_3 preparation was emphasized by H. Priest. Large porous nodules of trioxide are the most satisfactory (SAM-Columbia 4). Since UO_2 obtained by hydrogen reduction may readily be re-oxidized even at 40°C, it is necessary to keep it from contact with air. This is best achieved by proceeding with the hydrofluorination in the same apparatus immediately after reduction. Hydrofluorination is usually performed at 450°-550°C. It is a relatively slow reaction and its rate does not show much tem-

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*First used at Johns Hopkins University.

**An experimental determination of ΔH for the reaction in the range 600-800°C is -42.08 k cal (Los Alamos 1).

perature dependence above 350°C (M P Chicago 3). Temperatures as low as 400°C and as high as 650°C have been employed, but the optimum temperature appears to be close to 550°C. Above 700°C hydrofluorination is usually incomplete because of the rapid formation of an impervious layer of tetrafluoride on the oxide. The use of a large excess of hydrogen fluoride is recommended. The hydrofluorination reaction can be performed in copper, nickel, monel, aluminum or magnesium equipment. Nickel is probably the most satisfactory. Where a very pure product is required, the boat containing the uranium oxide should be protected by a graphite housing to prevent flakes of copper or nickel fluoride from falling into it. (CEW-TEC 3) Both stationary and rotating reactors have been used, depending on the amount of material to be treated. The time requirements are contingent on the scale of the operation; for 75 g batches of oxide reduction periods of ten hours and hydrofluorination periods of fifteen hours have been employed. Smaller quantities require less time. A systematic study of these variables has been made at the Tennessee Eastman Laboratories. The cycle recommended consists of a minimum of two hours reduction with hydrogen at 800°C, two hours hydrofluorination at 450°C, and two hours sintering at 875°C (CEW-TEC 4).

According to equations (26 and 27) either UO_2 or UO_3 is used as the initial material for the preparation of UF_4. The use of the easily available intermediate oxide, U_3O_8, depends on the completion of the reaction:

$$(28) \quad U_3O_8 + 2H_2 \longrightarrow 3UO_2 + 2H_2O$$

As described in Chapter 11 British investigators (British 27) have claimed that U_3O_8 cannot be reduced to $UO_{2.0}$ by hydrogen under the usually employed conditions (temperatures of 650°C-680°C and atmospheric pressure). The reduction product obtained under these conditions had the composition of $UO_{2.14}$ (or $UO_3 \cdot 6UO_2$); when treated with hydrogen fluoride, it yielded a mixture of uranium tetrafluoride and oxyfluoride:

$$(29) \quad UO_3 \cdot 6UO_2 + 26HF \longrightarrow UO_2F_2 + 6UF_4 + 13H_2O \, .$$

UO_2F_2 is a very undesirable impurity if the material is to be used in metal production.

Newer Tennessee Eastman Laboratory investigations indicate that the reduction of U_3O_8 stops at $UO_{2.14}$ only if the U_3O_8 has previously been subjected to temperatures above 800°C. If the U_3O_8 has not been heated so intensely during preparation, it is smoothly reduced to $UO_{2.0}$.

If U_3O_8 which may have been ignited above 800°C must be employed, for the preparation of UF_4, it is advisable to convert it first to uranyl nitrate and then to UO_3 by calcination at 300°C; or, the U_3O_8 may be converted directly to UO_3 by oxidation with N_2O_4.

For some purposes uranium tetrafluoride of high density is required. The density of the starting oxide is one of the major factors in determining the bulk density of the reaction product (CEW-TEC 5). As described in Chapter 11, the crystal characteristics of UO_3 depend on the mode of preparation. UO_3 of high bulk density can be prepared by treating U_3O_8 (ignited at 725°C and therefore dense) with N_2O_4 in the vapor phase. Such a material yields UO_2, and, indirectly, UF_4 of high density. Another method, which may be used to obtain UF_4 of high density, is to sinter the UF_4 at temperatures of 825°-875°C in an atmosphere of hydrogen fluoride (CEW-TEC 3). The sintering process, however, must be very carefully controlled since it seriously shortens the life of the metal reactors; losses by volatilization also can become troublesome at these high temperatures.

(b) Preparation of UF_4 By Reaction of UO_3 with Gaseous Ammonia and Hydrogen Fluoride. The Tennessee Eastman Laboratory has recently proposed a one-step process for the preparation of UF_4 which consists in passing a mixture of ammonia and hydrogen fluoride over uranium trioxide at 500°-750°C. (CEW-TEC 6) The reaction is very rapid, and produces UF_4 of high purity. From the point of view of the conversion yield, this ammonia-hydrogen fluoride procedure is distinctly superior to the one-step hydrogen-hydrogen fluoride reaction which has been advocated by various workers.

(c) Preparation of UF_4 by Reaction of Uranium Oxides with Fluorinated Hydrocarbons (Freons) at Elevated Temperatures. Many metal oxides can be converted to fluorides by reaction with fluorinated hydrocarbons (Ruff and Keim, 1931; Henne, 1938). Ergen, Heath, and Booth (1942) first examined the behavior of UO_3 in the presence of certain fluorinated hydrocarbons. Their results agree well with the later, more extended investigations of the Brown University Group, who have developed satisfactory methods for the preparation of UF_4 by the reaction of fluorinated hydrocarbons with various uranium oxides (Brown 3,4). The purity of the product obtained has not as yet been assessed, but the method appears to have certain advantages. The apparatus required is very simple; glass can be used although graphite is perhaps preferable. The reaction appears to be applicable to all oxides of uranium, and the product, which differs in physical characteristics from that obtained by the hydrogen fluoride procedure, may be more desirable for certain purposes.

The results obtained with a number of fluorinated hydrocarbons and various uranium oxides are given in Table 2. These experiments were performed in "Pyrex" and "Vycor" tubes. Calcium fluoride and polished graphite boats are suitable; because of its greater availability, graphite ware was used in most cases. The gaseous fluorocarbons were carefully dried by passage over phosphorous pentoxide since traces of moisture cause etching of the glass vessels during the initial stages of the reaction. The uranium oxides were dried by heating at 200-300°C either in vacuum or in a stream of dry nitrogen. In all cases a large excess of the fluorocarbons were used. In the case of liquid fluorocarbons, their vapors were delivered into the fluorination apparatus by a stream of dry nitrogen.

The most successful preparation was that which used UO_3 with dichlorotetrafluoroethane, $C_2Cl_2F_4$ (Freon 114), at 700°C. This fluorinated hydrocarbon corrodes silica to a lesser extent at high temperatures than any of the other materials investigated. UF_4 of good quality may also be prepared by the reaction of difluorodichloromethane (Freon 12) with UO_2, but the product has a lower bulk density than that obtained from Freon 114, and often adheres tenaciously to the boats. The product obtained from the freon reactions is almost free of chlorine, and very little volatilization of uranium-chlorine compounds occurs.

It has already been mentioned that polished graphite is the most suitable structural material for fluorination with fluorocarbons. Calcium fluoride is also suitable as a boat material although it seems to absorb UF_4 at high temperatures (Brown 5). Metals are attacked

TABLE 2

REACTIONS OF URANIUM OXIDES WITH FREONS

(Brown 4)

Compound	Commercial Names	B.P. °C.	Oxide		
			UO_2	UO_3	U_3O_8
CCl_3F	Freon 11	23.4	Reaction at 350°C. Product contained many soluble uranium chlorides.	Same as for UO_2. Graphite boats disintegrated rapidly.	-
CCl_2F_2*	Freon 12	-29.8	Fluorination proceeds fairly well even at 350°C. Low bulk density.	Rapid reaction at 400°C. Much sublimation from boats.	Same as for UO_3. Material adheres very firmly to boats.
$CHCl_2F$**	Freon 21	8.9	Undergoes extensive pyrolysis with much deposition of carbon.		
$C_2Cl_3F_3$	Freon 113	48	No reaction below 600°C. Incomplete after one hour at 600-650°C.	Same as for UO_2. Material adheres to boat very tenaciously.	-
$C_2Cl_2F_4$	Freon 114	3.5	Fairly satisfactory reaction at 675-700°C. Product has low bulk density.	Rapid at 650-700°C. High bulk density. Good conversion.	Reaction does not go to completion at 700°C.
C_7F_{16}	Coolant C-716	83	No reaction at 600°C.	Small amount of fluorination at 600°C.	-

*Seems to give more soluble chloride than does Freon 114.
**Ni tube used since HF was a possible by-product.

appreciably; nickel, copper, monel, platinum and stainless steels (Nos. 304 and 316) are all corroded, and, in addition, they promote pyrolysis with deposition of carbon. Silica ware is attacked to some extent, least of all by Freon 114 and Freon 12. In order to facilitate the reaction, a rotating kiln type of reactor has been constructed in which the reaction mass is kept in motion, continuously exposing fresh surface. A graphite tube is rotated in a silica tube fitted with a graphite liner to prevent attack on the silica (Brown 6).

The action on UO_3 of trichlorofluoromethane, CCl_3F (Freon 11), in the liquid phase also has been examined; reaction for seven hours at 120°C gave a 94 per cent yield of a water soluble product, presumably UO_2F_2 (Brown 3).

(d) Preparation of UF_4 from Uranium Metal or UH_3 by High Temperature Hydrofluorination. Uranium metal can be readily converted to uranium tetrafluoride by two general procedures. The first utilizes the two consecutive reactions:

(30) $U + 3/2\ H_2 \longrightarrow UH_3$

(31) $UH_3 + 4HF \longrightarrow UF_4 + 7/2\ H_2$

Massive uranium metal is first converted to the hydride at 250°C. To achieve complete conversion of the hydride to tetrafluoride, thorough agitation of the solid is necessary. A temperature of 200°C seems to be sufficient for the second step (M P Ames 3). However, in a static system, the reaction of hydrogen fluoride with uranium hydride at 270°C is very incomplete due to caking. If the hydride is decomposed at 500°C and the resulting finely divided metal is treated with hydrogen fluoride at the same temperature, it is claimed that good conversion to uranium tetrafluoride is obtained (M P Clinton 1).

The second procedure attempts to combine both steps into one. The simultaneous reaction of hydrogen and hydrogen fluoride with uranium metal has been investigated in some detail by the Ames Group (MP Ames 10). A mixture of approximately 50 mole per cent hydrogen and 50 mole per cent hydrogen fluoride will smoothly convert small quantities (50 g) of uranium metal to UF_4 at 250°C. Larger quantities of uranium cannot be treated in this simple way. The reaction between hydride and hydrogen fluoride takes place on the surface of the massive metal with the liberation of enough heat to raise the temperature to a point where the rate of hydride formation is negligible. (This rate falls off rapidly on approaching 430°C; See Chap. VIII.) Consequently, in order to allow the reaction to proceed, cooling to 350°C is necessary. When large quantities of metal are handled, mechanical agitation must be used to remove the uranium tetrafluoride scale as it forms (M P Ames 11). With these precautions the simultaneous reaction of hydrogen and hydrogen fluoride is now regarded as definitely superior to the step-wise reaction.

2.4 Miscellaneous Preparations of UF_4. The following reactions in which uranium tetrafluoride appears as a product are not important as preparative methods, but may be used in special cases.

(a) $UCl_3 + HF$. (CEW-TEC 1). At 450°C, uranium trichloride reacts with anhydrous HF:

$$(32) \quad UCl_3 + 4HF \longrightarrow UF_4 + 3HCl + 1/2\ H_2$$

(See reaction of UH_3 with HF, Chap. VIII Section 2.7a.) Note that tetrafluoride is formed rather than the trifluoride.

(b) $UO_2(HPO_4) \cdot H_2O + HF$ (CEW-TEC 7). At temperatures of 350-500°C uranyl fluoride, UO_2F_2, is the only product of reaction of uranyl phosphate and hydrogen fluoride. Above 500°C a rather unexpected reduction occurs, and at 800°C UF_4 is the main product obtained. The reaction is quite rapid.

(c) Uranium Oxides + Ammonium Fluoride (CEW-TEC 6 ; Mallinckrodt 1,2). UF_4 can be readily prepared by reaction of ammonium fluoride or bifluoride with UO_3:

$$(33) \quad 3UO_3 + 6NH_4HF_2 \longrightarrow 3UF_4 + 9H_2O + N_2 + 4NH_3$$

A temperature of 700°C is suitable. The product is free from ammonia. At lower temperatures (450°C) products of the type NH_4UF_5 are obtained. In carrying out this reaction, it is necessary to pass the ammonium fluoride vapor over the oxide; simple fusion is insufficient. The essential similarity between this procedure and that described above ($HF + NH_3$) is evident.

(d) $UCl_4 + HF_{(liq.)}$ (Brown 1). The reaction of UCl_4 and liquid anhydrous hydrogen fluoride proceeds quantitatively at room temperature to give a deep-green, crystalline product. The tetrafluoride obtained is found to retain considerable quantities of hydrogen fluoride which can not be entirely removed even by prolonged pumping at room temperature. Analysis of one sample indicated a composition close to $UF_4 \cdot HF$. If this material is heated (in a nickel tube fitted with a platinum liner) for a short time in vacuum (10^{-3} mm) at 625°C, a product entirely free of hydrogen fluoride can be obtained.

(e) UF_4 formation from UF_6. (See UF_6, Chapter XIII).

2.5 Physical Properties of Uranium Tetrafluoride. (a) Melting Point. A melting point of 960° ± 5°C is derived from the plateau on the heating curve of UF_4 determined by an optical pyrometer (M P Chicago 4).

(b) Volatility. No reliable vapor pressure data are available. A single value of 1.9×10^{-4} mm at 760°C obtained in the course of other work (M P Chicago 5), appears to be consistent with the general properties of UF_4. Uranium tetrafluoride is not appreciably volatile in dry nitrogen at 800°-880°C; the small amount of volatilization actually observed can be attributed to the presence of UO_2F_2 (Brown 4). British workers have purified the tetrafluoride by vacuum sublimation (British 2): A high vacuum (10^{-6} mm Hg) and a temperature of 1000°C are required. A silica tube equipped with a molybdenum metal liner was used. For large quantities, a length of stainless steel tubing provides a suitable distillation apparatus.

(c) Crystallography, X-Ray Structure, and Density. Uranium tetrafluoride obtained by vacuum sublimation at 1000°C consists of green, needle-like crystals up to several millimeters in length and up to 0.5 mm in diameter. Most of them appear twinned parallel to the length of the needle. They often show between crossed Nichols an imperfect extinction which changes from one region to another, and is probably due to distortions. The crystals are triclinic. All of the crystals are twinned so that monoclinic symmetry is simulated. Goniometric study of a pseudo-monoclinic crystal showing (310) and (111) faces yielded the following axial ratios and angle: a:b:c = 1.282:1:1.760 (± 0.001); $\beta = 98^{\circ}49 \pm 2.'$

TABLE 3

REFRACTIVE INDICES AND PLEOCHROISM OF UF_4 CRYSTALS

(British 3)

Crystallographic direction	N	Pleochroic Color
α	1.500	very light green, nearly colorless
β	1.585	emerald green
γ	1.598	emerald green

X-ray photographs of small single crystals of uranium tetrafluoride show monoclinic symmetry with twelve molecules per unit cell. The approximate lattice dimensions are:

$a_1 = 12.79 \pm 0.06A$ $a_2 = 10.72 \pm 0.05A$

$a_3 = 8.39 \pm 0.05A$ $\alpha_2 = 126^{\circ}10 \pm 40'$

The space group is C 2/c (C_2h^6). UF_4 is thus isomorphous with ThF_4 CeF_4, ZrF_4, and HfF_4 (M P Chicago 6). The x-ray structure of anhydrous UF_4 is the same, whether the material is prepared from aqueous solution, or obtained by high temperature hydrofluorination.

The density calculated from the x-ray data is 6.70 ± 0.10g/cc. The density of uranium tetrafluoride determined by immersion in alcohol has been reported as 6.95g/cc (British 28) and 6.43g/cc (SAM- Columbia 5). Values of bulk density varying from 1.50 to 3.5g/cc have been observed. As has already been mentioned, the bulk density of UF_4 prepared from aqueous solution and dried below 500°C is, in general, considerably lower than that of uranium tetrafluoride prepared by high temperature reactions.

No data appear to be available on the structure of the monohydrate, $UF_4 \cdot H_2O$. The hydrate, $2UF_4 \cdot 5H_2O$ is orthorhombic with eight molecules per unit cell (M P Chicago 6,7):

$$a_1 = 12.75 \pm 0.04A, \quad a_2 = 11.12 \pm 0.04A, \quad a_3 = 7.05 \pm 0.03A$$

The computed density is 4.74g/cc. The atomic positions are:

$4\ U_I$ in $(x_1 y_1 \frac{1}{4})$ $(x_1 + \frac{1}{2}, \frac{1}{2} - y_1, \frac{1}{4})$

with $x_1 = 0.055$, $y_1 = 0.14$

$4\ U_{II}$ in $\pm (x_2 y_2 \frac{1}{4})$ $(x_2 + \frac{1}{2}, \frac{1}{2} - y_2, \frac{1}{4})$

with $x_2 = -0.025$, $y_2 = -0.139$

The space group is Pnam.

(d) Thermodynamic Data. The specific heat, enthalpy and entropy of UF_4 from 20°K to 350°K have been determined (Nat. Bur. Standards 1). The sample of UF_4 used contained 2 per cent UO_2F_2; if the heat capacities of UF_4 and UO_2F_2 do not differ by more than 10 per cent, an error of only 0.2 per cent could be caused by this impurity. The calorimeter was of the adiabatic type (Southard and Brickwedde 1933). The C_p values given in Table 4 were obtained from a smooth curve laid through the experimental points. (See Fig. 2)

The following thermochemical data have been obtained at Columbia (SAM-Columbia 6) for the formation of UF_4:

(34) $U_{(solid)} + 2F_{2(g)} \longrightarrow UF_{4(solid)}$

$-\Delta H_{298} = 446 \pm 2$kcal/mole

Using the UF_4-entropy value of 36.13 e.u. (= 151 j/°k) at 298°C from Table 4 together with the entropy value for U and F_2, one calculates:

(34a) $-\Delta F_{298} = 424.6$ kcal/mole.

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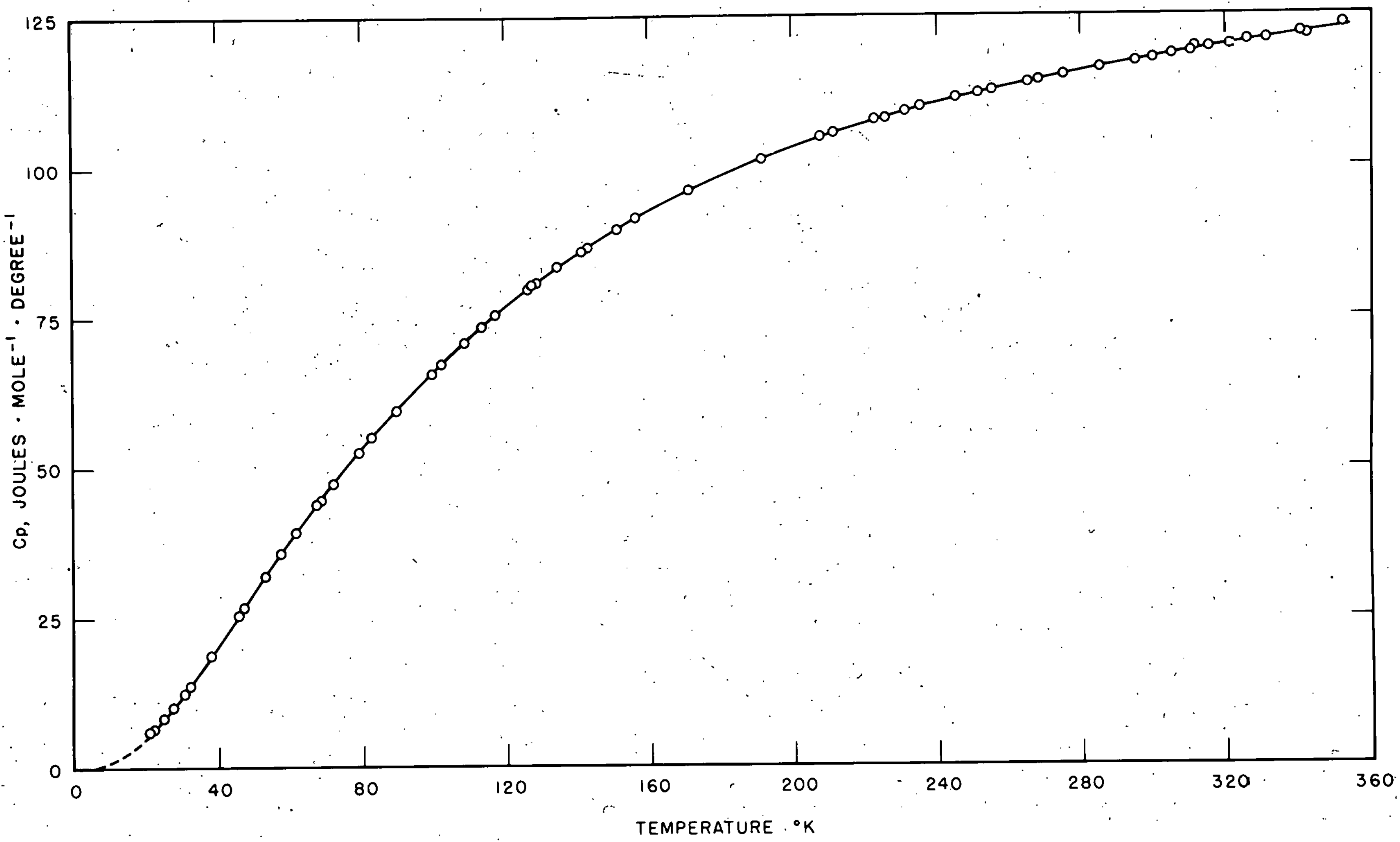

FIG. 2. SPECIFIC HEAT OF URANIUM TETRAFLUORIDE FROM 20° TO 350° K.

TABLE 4 *

SPECIFIC HEAT, ENTROPY, AND ENTHALPY OF UF_4

$$S-S_o = \int_0^T (C_p/T)\, dT \qquad H-H_o = \int_0^T C_p dT$$

$T\ ^oK$	C_p (joules/mole °K)	$S-S_o$ (joules/mole °K)	$H-H_o$ (joules/mole)
20	5.13	1.7	26.1
22.5	6.34		
25.0	7.93	3.2	58.1
27.5	9.84		
30	11.80	4.9	107.3
32.5	13.98		
35	16.15	7.1	177.2
37.5	18.30		
40	20.49	9.5	268.8
45	24.84		
50	29.22	15.0	517.2
55	33.51		
60	37.72	21.1	852
65	41.84		
70	45.81	27.6	1270
75	49.55		
80	53.14	34.2	17.6
85	56.59		
90	59.88	40.8	2331
95	63.00		
100	65.96	47.4	2961
105	68.84		
110	71.60	54.0	3649
115	74.28		
120	76.76	60.5	4391
125	79.19		
130	81.50	66.8	5183
135	83.66		

TABLE 4 (cont'd)

SPECIFIC HEAT ENTROPY AND ENTHALPY OF UF_4

T^oK	C_p (joules/mole °K)	$S-S_o$ (joules/mole °K)	$H-H_o$ (joule/mole)
140	85.66	73.0	6020
145	87.57		
150	89.39	79.0	6895
155	91.14		
160	92.83	84.9	7806
165	94.42		
170	95.92	90.6	8750
175	97.33		
180	98.66	96.2	9724
185	99.93		
190	101.12	101.6	10,273
195	102.24		
200	103.32	106.8	11,745
205	104.36		
210	105.35	111.9	12,789
215	106.32		
220	107.24	116.9	13,852
225	108.10		
230	108.92	121.7	14,933
235	109.71		
240	110.47	126.3	16,030
245	111.20		
250	111.89	130.9	17,142
255	112.56		
260	113.20	135.3	18,267
265	113.81		
270	114.41	139.6	19,405
273.16	114.80	140.9	19,767
275	115.03		

TABLE 4 (cont'd)

SPECIFIC HEAT ENTROPY AND ENTHALPY OF UF_4

T°K	C_p (joules/mole °K)	$S-S_o$ (joules/mole °K)	$H-H_o$ (joules/mole)
280	115.63	143.8	20,556
285	116.20		
290	116.75	147.8	21,717
295	117.28		
298.16	117.62	151.1	22,674
300	117.81	151.8	22,890
305	118.33		
310	118.84	155.7	24,074
315	119.35		
320	119.85	159.5	25,267
325	120.33		
330	120.81	163	26,470
335	121.28		
340	121.74	166.8	26,683
345	122.20		
350	122.64	170.4	28,905

*The heat capacity data were extrapolated to 0°K by the equation:

$$C_p = 3R\left[D + 4.1 \times 10^{-6}T^3\right] \text{ joules/mole °K},$$ where
D = is the Debye Function, with θ = 150°K.

The above value of ΔH is obtained by measuring the heat of solution of $U(SO_4)_2$, the heat of formation of $UF_4.H_2O$ in aqueous solution, and the heat of hydration of UF_4 and combining them with the heats of formation of $U(SO_4)_2$, $SO_4^{=}$ and $F^{=}$ found in the literature (Table 4A):

TABLE 4A

THERMODYNAMIC FUNCTIONS

Equation No.	Reaction	ΔH_{298} for UF_4 (kcal/mole)
(35)	$U(SO_4)_{2(solid)} \rightarrow U(IV)_{(aq)} + 2SO^{=}_{4(aq)}$	-24.1 ± 0.2
(36)	$U + 2S + 4O_2 \rightarrow U(SO_4)_2$	-534.
(37)	$U(IV)_{(aq)} + 4F^{-}_{aq} + H_2O \rightarrow UF_4 \cdot H_2O_{(solid)}$	-10.3 ± 0.2
(38)	$UF_4 \cdot H_2O_{(solid)} \rightarrow UF_{4(solid)} + H_2O$	+3.3 ± 0.3
(39)	$2SO^{=}_4 \rightarrow 2S_{(solid)} + 4O_2$	+431.6
(40)	$2F_2 \rightarrow 4F^{-}_{(aq)}$	-312.8

Because of the importance of the values (34) and (34a) have been redetermined (SAM-Carbide and Carbon 1) by a different method. Uranium tetrachloride (solid) was converted to hydrated UF_4 (s) with excess KF solution, and the heat of hydration of UF_4 (surface area = 6 m^2/g) was measured in a KF solution of the same concentration. A value of -444 ± 2.5 kcal/mole was obtained for the heat of formation of UF_4. We may consider the average of the two determinations, $\Delta H = -443.5$ kcal/mole, as the most probable value. It agrees quite well with that obtained from a study of the high temperature hydrolysis of UF_4 (Los Alamos 1).

(e) Thermal Conductivity of Solid UF_4. The thermal conductivity of fused uranium tetrafluoride has been given as 0.0047 ± 4.3 per cent (cal/cm sec°C)at 60°C (M P Chicago 8).

2.6 Chemical Properties of Uranium Tetrafluoride. Uranium tetrafluoride is a green, crystalline solid. Material prepared by high temperature reactions usually is darker, denser, and much less hygroscopic than uranium tetrafluoride prepared by Grosse's method (SAM-Columbia 2). Chemically, uranium tetrafluoride may in general be considered a stable, rather inert substance. In its physical properties, it resembles other tetravalent fluorides, particularly the isomorphous compounds ZrF_4, HfF_4, and ThF_4. The chemical differences arise principally from the fact that uranium can exist in a number of different valence states whereas the other elements are exclusively tetravalent.

(a) Water. The solubility of UF_4 in water at 25°C is approximately 0.10 g or 0.14 millimoles per liter (SAM-Columbia 2). Its molar solubility is thus of the same order of magnitude as that of calcium fluoride. British workers reported a solubility of 600 mg/l (British 29). The most reliable values for the solubility of UF_4 in H_2O probably are those of the SAM-Carbide and Carbon Laboratories (SAM-Carbide and Carbon 2). They give the solubility at 25°C as 0.004 per cent by weight of UF_4, corresponding to 10^{-4} mole/liter; the solubility at 0°C is 3×10^{-5} mole/liter and at 60°C, 4×10^{-4} mole/liter. The solubility increases when hydrofluoric acid is added to water to about 0.03 g UF_4 per 100 g solution at a hydrofluoric acid concentration of 30 weight per cent. Whether uranium tetrafluoride reacts with water (apart from hydration)is still doubtful. British workers (British 30) state that uranium tetrafluoride does not lose fluorine when boiled with water for extended periods of time (seventy-two hours), and that no hydrolysis occurs. Other workers (Dupont 1) state that as much as 85 per cent will decompose and go into solution at room temperature in twenty-four hours, and that considerable reaction occurs at the boiling point in one hour. Analysis showed that the uranium in such solutions was no longer in the tetravalent atate. One reason for the discrepancy may be that whereas British workers used 5.0 g/100 cc the other group used only 0.3 g/100 cc of tetrafluoride, and the amount of dissolved oxygen in water may have been sufficient to oxidize an appreciable fraction of the smaller sample. In any event it is known that very small amounts of excess hydrofluoric acid repress hydrolysis, as evidenced by the successful precipitation of the tetrafluoride from boiling aqueous solution. No basic uranium flourides are known.

(b) Water Vapor. Anhydrous UF_4 is not appreciably hydroscopic in air at room temperature. In one case an increase in weight of 0.05 per cent in five hundred and sixty-four hours was observed (British 31). The previous history of the uranium tetrafluoride is of importance in this connection since material prepared from aqueous solutions, particularly by dehydration of $2UF_4.5H_2O$, is much more hygroscopic than UF_4 prepared by high temperature hydrofluorination.

(c) Steam. A direct determination of the equilibrium constant of the reaction

$$(41) \quad UO_2 + 4HF \rightleftharpoons UF_4 + 2H_2O$$

has been made in the range 600°-800°C (Los Alamos 1). The results are summarized in Table 5. The heat of reaction, which is sensibly constant in this temperature range, is calculated to be $\Delta H = -42.08$ kcal.

It is obvious that if uranium tetrafluoride is treated with steam under such conditions that the hydrogen fluoride produced is swept out of the system, the tetrafluoride will be converted to UO_2. The equilibrium constants show that hydrolysis of the UF_4 will be markedly enhanced with increasing temperatures.

TABLE 5

EQUILIBRIUM CONSTANTS FOR THE HYDROFLUORINATION OF UO_2

$$K = \frac{p_{H_2O}^2}{p_{HF}^4}$$

$T^\circ C$	$100/T^\circ_K$	K	ln K
600	1.145	14.0	2.639
705	1.021	1.47	0.385
800	0.932	0.155	-1.865

$$\ln K = \frac{42080}{RT_{^\circ K}} - 21.5$$

The heats of hydrolysis of a number of bivalent and trivalent fluorides have been determined by Domange (1937). The thermodynamic data available are not sufficiently extensive to make possible a detailed comparison of the free energies of hydrolysis of all the metal fluorides. However, in a general way, all metal fluorides fall into two categories with respect to ease of hydrolysis: (a) Difficultly hydrolyzable fluorides of uni- and bivalent cations, such as NaF, KF, CuF_2, and BeF_2; (b) readily hydrolyzable fluorides of tri- and tetravalent cations, such as LaF_3, AlF_3, ThF_4, and UF_4. Extrapolation of the free energy of the hydrolytic reaction of UF_4 to 500°C, leads to a value of $\Delta F_{500^\circ C} = +2.8$ kcal. This small value indicates the necessity of maintaining a hydrogen fluoride atmosphere when hydrated UF_4 is being dried at 500°C , and suggest that the dehydration should preferably be carried out at lower temperatures.

The dehydration of hydrated UF_4 is further complicated by the extreme sensitivity of the system to traces of oxygen. Should the dehydration process be long continued and should even traces of oxygen be allowed access to the UF_4, oxidation to uranyl fluoride will occur. Once oxygenation has occurred, no amount of further treatment with hydrogen fluoride will remove the oxygen (British 26; Dupont 1).

(42) $UF_4 + HOH \rightleftharpoons UF_3(OH) + HF$

(43) $UF_3(OH) + HOH \rightleftharpoons UF_2(OH)_2 + HF$

(44) $2UF_2(OH)_2 + O_2 \longrightarrow 2UO_2F_2 + 2H_2O$

The hydrolytic conversion of UF_4 to uranium oxides has been adapted as an analytical method for the determination of fluorine in UF_4 (M P Ames 12). Complete hydrolysis is achieved by the use of superheated steam at 900°C in a platinum apparatus. The steam is first superheated in a quartz heater; the hydrofluoric acid is collected in a platinum condenser and determined by titration.

In an interesting extension of this work it has been found that fluorides(and chlorides) which are normally difficult to hydrolyze can be readily decomposed by steam at 1000°C if mixed with U_3O_8. The equilibrium is shifted to such an extent that substances such as KF or CaF_2 undergo hydrolysis very rapidly under these conditions (M P Ames 13, 14).

(d) Oxidizing Agents. Early workers reported UF_4 to be converted to U_3O_8 by ignition in air, and noted that if free access of air was prevented (heating in a covered crucible), UO_2F_2 would be obtained (Bolton, 1866; Smithells, 1883). More recently UF_4 has been reported to be comparatively stable in air on heating for short periods at 200°C. At higher temperatures decomposition is considerable (British 25; Dupont 1). The behavior of UF_4 in pure, dry oxygen has been investigated more recently, with very interesting results (M P Chicago 9; Brown 4). At 800°C the following reaction has been shown to occur:

(45) $2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2$

By working in metallic apparatus the UF_6 can be collected. (A detailed discussion of this reaction will be found in Chapter XIII in the section dealing with the preparation of UF_6). These observations show that ignition of UF_4 in dry air is inadvisable since appreciable amounts of uranium may be lost as the volatile hexafluoride.

Chlorine. (Brown 4; M P Ames 15). Chlorine has very little effect on UF_4 at 500°-675°C; the slight reaction observed can be attributed to oxygen present in the chlorine. A solution of chlorine in carbon tetrachloride has no effect on UF_4 at 125°-130°C (nine hours under pressure). The addition of UCl_5 has no effect on this reaction (Brown 7). Fluorine reacts with UF_4 above 250°C to give the hexafluoride (M P Chicago 3). (See Chapter XIII)

(46) $UF_4 + F_2 \rightarrow UF_6$

Cobaltic Fluoride. CoF_3 converts UF_4 to UF_6; antimony pentafluoride, SbF_5, (Dupont 2) on the other hand, forms an equimolar complex with uranium tetrafluoride which is thermally stable up to 200°C in vacuum. When the complex is heated to 650°C, no noticeable quantities of volatile uranium compounds are produced; instead, 15 to 20 per cent of water-soluble uranium compounds are found in the residue. The complex decomposes in water to give insoluble uranium tetrafluoride and soluble antimony salts.

Oxidizing acids dissolve UF_4 rapidly to give uranyl ion solution. Fuming perchloric acid is one of the best reagents for dissolving the tetrafluoride. Nitric acid attacks UF_4 only very slowly; the addition of boric acid (DuPont 1) enhances the solvent action of nitric acid (as well as of other acids) by removing fluoride ions as they form:

(47) $2UF_4 + 2H_3BO_3 + 6HNO_3 \rightarrow 2UO_2(NO_3)_2 + 2HBF_4 + N_2O_3 + 5H_2O$

Other strong oxidizing agents react with UF_4 to give solutions of soluble uranyl salts. Thus, ceric sulfate solution dissolves UF_4; alkali peroxides (Na_2O_2) and ammonia - H_2O_2 mixtures react vigorously with UF_4, yielding soluble peroxyuranates. The reaction with ammonia-H_2O_2 is very vigorous and must be carefully regulated. The H_2O_2 is added to a suspension of UF_4 in 1:1 NH_4OH at such a rate that the solution is maintained just boiling (CEW-TEC 2).

Ferric salts, ($FeCl_3$, FeF_3)react with UF_4 with the formation of uranyl solutions; the complexing of fluoride by iron accelerates the reaction. Low pH seems to favor the oxidation and dissolution of UF_4 by FeF_3 British 29). Uranium tetrafluoride also dissolves readily in boiling aluminum nitrate or aluminum chloride solution, presumably by virtue of the formation of stable aluminum fluoride complex ions, such as AlF_6^{-3}. The uranium is simultaneously oxidized to the hexavalent state (CEW-TEC 8).

The conversion of UF_4 to U_3O_8 by fusion with salts (M P Ames 16) has been studied. The following salts yield easily soluble products which, however, still contain fluorine: KIO_3, $KBrO_3$, $KClO_3$, and mixtures of $KClO_3$ and $KHSO_4$. The most satisfactory agent for this conversion is KNO_3. The following salts yield easily soluble products from which the fluorine is volatilized away: $(NH_4)NO_3$, $(NH_4)_2C_2O_4 \cdot H_2O$, HIO_3, $(NH_4)_2S_2O_8$, and NH_4Br. Ammonium oxalate is stated to be the most efficient reagent in this group. Boric acid fusion also finds frequent use in converting UF_4 to U_3O_8. Uranium tetrafluoride undergoes reaction with uranium hexafluoride, UF_6 (See the preparation of U_2F_9, UF_5 and U_4F_{17} Section 3 of this Chapter).

(e) Reaction of UF_4 in which Uranium Remains Tetravalent. UF_4 is scarcely attacked by cold concentrated hydrochloric, sulfuric, phosphoric, or perchloric acid. In hydrochloric acid solutions the solubility becomes quite large with increasing HCl concentration. Thus, 0.18 per cent of UF_4 may be dissolved in 1 N HCl, 1.1 per cent in 6 N HCl, and 3.6 per cent in 12 N HCl. The addition of boric acid, as has been mentioned above, greatly accelerates the attack of these acids yielding corresponding solutions of U(IV). Fuming with sulfuric acid leads to solution on subsequent dilution with water (CEW-TEC 2) (c.f. above p.).

A mixture of dilute sulfuric acid and silica dissolves UF_4 quite readily with the formation of $U(SO_4)_2$ solution and fluosilicic acid. Hot Phosphoric acid dissolves UF_4 to give U(IV) phosphate. UF_4 is also moderately soluble in ammonium oxalate (0.4) per cent) solution. On heating UF_4 with sodium hydroxide solution "metathesis" to a hydrated oxide, $UO_2 \cdot x\ H_2O$, occurs (Bolton, 1866).

Uranium tetrafluoride reacts with anhydrous aluminum chloride at elevated temperatures to form uranium tetrachloride (M P Chicago 10):

(48) $$3UF_4 + 4AlCl_3 \xrightarrow{250^\circ-500^\circ C} 3UCl_4 + 4AlF_3$$

The double salt, $NaAlCl_4$, can also be used for this purpose (CEW-TEC 9). This is an excellent method for preparing uranium tetrachloride directly from the tetrafluoride without preparing the oxide as an intermediate. The metal chlorides, HCl, $SiCl_4$, $MnCl_2$, $ZnCl_2$, as may be anticipated from thermochemical considerations, fail to react.

(f) Reducing Agents. Pure hydrogen reduces UF_4 at 1000°C to UF_3 (see Section 1 of this Chapter). Atomic hydrogen (M P Chicago 11) at 700°C gives a mixture of UF_3 and UO_2 owing to the presence of traces of moisture from the attack of atomic hydrogen on the quartz reaction vessel.

Metallic uranium reduces UF_4 to UF_3. (See Sec. 1.1b) Alkali metals reduce UF_4 to uranium metal as do the alkaline earth metals, particularly calcium and magnesium. (See Chapter IV). Electrolytic reduction of molten UF_4-NaF also yields uranium metal (Los Alamos 2). (See Chapter IV)

(g) Complex Compounds of UF_4. Uranium tetrafluoride forms a series of double salts with metal fluorides. Compounds of this type were first encountered at an early stage in the development of uranium chemistry. Thus, in 1866 Bolton observed the formation of a green, water-insoluble compound when a uranyl fluoride solution containing potassium fluoride and formic acid was exposed to strong sunlight (Bolton, 1866). Photochemical reduction of solutions of uranyl ion containing sodium or potassium fluoride can also be effected (in the presence of sunlight) with alcohol, ether, or glucose (Aloy and Rodier, 1922). In each case a green substance, resembling UF_4 rather closely in appearance, is produced. The compound melts in air with evolution of hydrogen fluoride; after long continued heating, a residue of potassium or sodium uranate remains. The complex salts react only slowly with dry hydrogen, are practically insoluble in water or dilute acids, dissolve slowly in concentrated hydrochloric acid, and dissolve in hot concentrated sulfuric acid with evolution of hydrogen fluoride. Early workers formulated these compounds as $NaUF_5$ and KUF_5.

The system NaF-UF_4 has more recently received closer study (Brown 8). The methods of thermal analysis were employed, and it was reported that only one compound, $NaUF_5$ (m.p. 714° ± 10°C) existed. Two eutectic mixtures were detected, one NaF-$NaUF_5$ (m.p. 600° ± 10°C) at 26 mole per cent of UF_4, the other $NaUF_5$-UF_4 (m.p. 650° ± 10°C) at 67 mole per cent of UF_4.

Later the system $NaF-UF_4$ was re-examined by x-ray crystallographic techniques, and it is certain from this study that this and other similar systems are much more complex than had previously been assumed (M P Chicago 12). The x-ray data indicate the existence of no less than five phases (Table 6).

The systems studied were prepared by melting the components together rapidly in a platinum vessel and allowing them to cool. In some cases the melts were quenched. The phases, as indicated above, were identified by x-ray methods.

$NaUF_5$. This phase is rhombohedral. The unit cell contains six molecules with the following lattice dimensions:

$a = 9.08 \pm 0.01 Å$; $\alpha = 107° 56'$

The calculated density is 5.81.

The space group is $R\bar{3}$ (C_{3i}^2). In the unit cell one set of six sodium atoms, one set of six uranium atoms, and five sets of fluorine atoms are in positions $\pm$ (xyz)(yzx)(zxy) with parameters:

	x	y	z
Na	6/13	2/13	5/13
U	3/13	1/13	9/13

The arrangement of the sodium and uranium atoms is that of a face-centered, pseudo-cubic lattice in which every thirteenth site is vacant. The pseudo-cell is a rhombohedron with a volume 4/13 that of the true cell, and dimensions

$a = 5.72 Å$ and $\alpha = 90° 51'$.

The structure of Na_2UF_5 is closely related to flucrite.

α-Na_2UF_6. The chemical composition of this phase can be expressed as

TABLE 6

PHASE RELATIONSHIPS IN THE NaF-UF_4 SYSTEM

Mole Per Cent UF_4	Phases Present
67	UF_4 + $NaUF_5$
50	$NaUF_5$
40	a. αNa_2UF_6 + trace $NaUF_5$
	b. αNa_2UF_6
36	αNa_2UF_6
33	a. αNa_2UF_6 + γNa_2UF_6
	b. γNa_2UF_6
	c. βNa_2UF_6 + γNa_2UF_6
31	γNa_2UF_6
29	Na_3UF_7
27	Na_3UF_7
25	Na_3UF_7
20	Na_3UF_7 + NaF

$Na_{4-x}U_xF_{4+3x}$, where x can have values between 1.33 (corresponding to Na_2UF_6) and 1.60.

The phase is cubic face-centered. The lattice constants vary with the value of x:

x	a	ρ (g/cc)
1.33	5.565±0.005 A	5.08
1.45	5.579±0.005	5.35
1.60	5.002±0.001	5.66

This substance has a disordered structure of the fluorite type. In each unit cell there are four Na+U atoms distributed at randon over the sites (000) $(\frac{1}{2}\frac{1}{2}0)(\frac{1}{2}0\frac{1}{2}))$ $(0\frac{1}{2}\frac{1}{2})$. There are also 8.0-8.8 fluorine atoms per unit cell. Of these, eight fluorine atoms are at ± (1/4 1/4 1/4) (1/4 3/4 3/4) (3/4 1/4 3/4) (3/4 3/4 1/4), that is, they occupy the anion sites of the fluorite structure. The excess fluorine atoms are distributed at random over the sites $(00\frac{1}{2})$ $(0\frac{1}{2}0)$ $(\frac{1}{2}00)$ $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. This structure becomes unstable relative to $NaUF_5$ if more than 20 per cent of these sites are occupied.

β-Na_2UF_6. When melts of the composition Na_2UF_6 are quenched, the product consists of two phases, α-Na_2UF_6, and the new phase β-Na_2UF_6. β-Na_2UF_6 has hexagonal sysmmetry:

$$a_1 = 5.94 + 0.01 \text{ A} \qquad a_3 = 3.74 \pm 0.01 \text{ A} .$$

There is one moleculo per unit cell, and the calculated density is 5.74 g/cc The space group is $C_31m(D_{3d}{}')$. Each metal atom is bound to six fluorine atoms. The occupied positions are:

2Na in ± (1/3 2/3 1/2)
1U in (000)
6F in ± (u0v) (0uv)(uuv), where $u = 0.33$
$v = 0.23$

γ-Na_2UF_6. The chemical composition of this phase is sharply defined, and the compound is obtained in pure form when melts of this composition are cooled without quenching. The phase exhibits orthorhombic symmetry, with

$$a_1 = 5.56 \pm 0.02 \text{ A}, \quad a_2 = 4.01 \pm 0.01 \text{ A}, \quad a_3 = 11.64 \pm 0.04 \text{ A}$$

There are two molecules per unit cell, and the calculated density is 5.06 g/cc.

Na_3UF_7. The chemical formula for this phase can be expressed as $(Na_{6-x} + U_x)\ U_2F_{14+3x}$ with x in the range $0 < x < 0.30$. For x = 0 the composition is Na_3UF_7. The phase is tetragonal, and the lattice periods vary with x. For the extreme ends of the range the parameters are:

x	a_1	a_3	ρ (g/cc)
0	5.448 ± 0.007 A	10.896 ± 0.014 A	4.49
0.29	5.503 ± 0.005 A	11.006 ± 0.010 A	4.85

The space group is $14/mmm$ (D_{4h}^{17}). Each metal atom is linked to an average of 7.0 - 7.4 fluorine atoms with Na-F = U-F=2.36 -2.38 $\mathring{A}$. The unit cell and structure of Na_3UF_7 correspond to two fluorite unit cells placed one on top of the other, with uranium atoms occupying one fourth and sodium atoms occupying three-fourths of the metal sites. Two of the sixteen fluorine atoms are removed. All of the phases described are closely related structurally.

A similar study has been made of the KF-UF_4 system (M P Chicago 13). In addition to the terminal pure phases, eight phases were found, and the actual chemical formulas of the phases were deduced from the x-ray data. Table 7 gives the phase composition of melts in the system KF-UF_4.

The x-ray crystallographic data relating to these phases are summarized in Table 8.

By precipitation from aqueous solution, a series of compounds of the type MUF_6 (M = Ba, Pb, Sr) have been prepared. All of these compounds have the LaF_3-type of structure with the following lattice dimensions (M P Chicago 14):

	a_1	a_3
$BaUF_6$	4.265 ± 0.005 A	7.456 ± 0.015 A
$PbUF_6$	4.175 ± 0.005	7.337 ± 0.015
$SrUF_6$	4.103 ± 0.005	7.290 ± 0.015

Because of their low melting points (as compared to UF_4), the NaF-UF_4 and KF-UF_4 systems have received much attention as possible electrolytes for the preparation of uranium metal by high temperature electrochemical methods. (See Chapter IV)

TABLE 7

PHASE COMPOSITIONS IN THE SYSTEM KF-UF_4

	PHASE PRESENT		
Atom Per Cent of UF_4	Major Phase	Minor Phase	Trace
89	KU_6F_{25} + UF_4		
86	KU_6F_{25}	KU_2F_9 + UF_4	
83	KU_6F_{25}	KU_2F_9	UF_4
80	KU_2F_9 + KU_6F_{25}		UF_4 + KU_3F_{13}
75	KU_2F_9 +KU_6F_{25}		KU_3F_{13} +UF_4
67	KU_2F_9		KU_6F_{25}+ $KU_{13}F_3$+ KUF_5
60	KU_2F_9+ KUF_5		
50	KUF_5		
45	KUF_5	β-K_2UF_6	
40	KUF_5+ β-K_2UF_6		
36	β-K_2UF_6	α-K_2UF_6	
33	β-K_2UF_6+ β"K_2UF_6		α-K_2UF_6
29	β-K_2UF_6+ αK_3UF_7		
20	α-K_3UF_7		KF
14	α-K_3UF_7	KF	

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TABLE 8

CRYSTALLOGRAPHIC DATA OF THE SYSTEM $KF-UF_4$

Phase	Symmetry	Lattice Dimensions (A°)			No. of Molecules per unit cell	Density (g/cc)	Space Group
		a_1	a_2	a_3			
KU_6F_{25}	Hexagonal	8.18±0.01		16.42±0.02	2	6.73	C6/mmc
KU_3F_{13}	Orthorhombic	8.03±0.03	7.25±0.03	8.53±0.04	2	6.64	Pmcm
KU_2F_9	Orthorhombic	8.68±0.01	7.02±0.01	11.44±0.04	4	6.49	Pnam
KUF_5	Rhombohedral	9.387±0.002	α=107°15' ±2'		6	5.38	$R\bar{3}$
α-K_2UF_6	Cubic Face Centered	5.934±0.001				4.53	Fluorite Structure
β-K_2UF_6	Hexagonal	6.54±0.01		3.76±0.01	1	5.10	C62M Ordered
β'-K_2UF_6	Hexagonal	6.54±0.01		3.80±0.01	1	5.05	C62m Complete Disorder
β''-K_2UF_6	Hexagonal	6.53±0.02		4.04±0.01	1	4.77	$C\bar{3}1m$
α-K_3UF_7	Cubic Face-centered	9.21±0.01			4	4.12	Probably A Disordered Structure
β-K_3UF_7	Tetragonal				8	4.13	I4/amd

3. Uranium Pentafluoride, UF_5, and the Intermediate Fluorides U_2F_9 and U_4F_{17}

Uranium pentafluoride was first described by Ruff and Heinzelmann (1911) who prepared it by the reaction of anhydrous hydrogen fluoride with uranium pentachloride. For a long time this was the only known compound with a comparison between UF_4 and UF_6. Recent work at the S.A.M. Laboratories of Carbide and Carbon Chemical Corporation has shown that at least two intermediate compounds exist between UF_4 and UF_5; they have been assigned the formulae U_2F_9 and U_4F_{17}. The discovery of these compounds arose from the study of the reaction between uranium tetrafluoride and uranium hexafluoride which proved unexpectedly complex.

3.1 Historical. In 1941 Grosse (SAM-Columbia 7,8) proposed the following reaction for the preparation of uranium pentafluoride:

(49) $UF_4 + UF_6 \xrightarrow{125°C} 2UF_5$

An attempted preparation of UF_5 by this procedure at Chicago yielded a black product instead of the expected white or grey one (M P Chicago 15). Chemical analysis indicated the black substance possessed the approximate formula UF_4 but x-ray analysis (M P Chicago 1) showed it to be cubic ($a_o = 8.455 \mathring{A}$) while UF_4 is monoclinic and UF_5 tetragonal. Volume considerations, based on the ionic radius of F^- in other uranium compounds, indicated that the atomic ratio F/U in the black substance was 4 ± 0.3. It was therefore suggested that this new substance was a crystal modification of UF_4, and it received the designation "black UF_4". Some support was given to this view by the observation that "black UF_4" was converted to ordinary UF_4 on standing or by moderate heating after inoculation with a crystal of monoclinic UF_4 (M P Chicago 16).

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Once attention was directed to the "black fluoride," it was soon realized that a substance of this character is formed under a wide variety of circumstances. Thus, when a mixture of UF_6 and hydrogen was passed through a hot tube (400-600°C), a small amount of a jet black solid was obtained with a composition approximating UF_4. In this case, too, it was concluded that a new crystal modification of UF_4 had been found (M P Ames 17).

A similar substance was encountered by British workers in the course of corrosion studies. Mild steel samples exposed to UF_6 vapor formed a black scale with the composition $FeF_2 \cdot 2UF_5$ (or $FeF_3 \cdot U_2F_9$)(British 32). These workers also studied what was referred to as a "UF_4-UF_6 complex" This complex was prepared by treating UF_4 with liquid UF_6 at 150°-$200^\circ C$; it was a brown powder which appeared to have the composition $UF_{4.4}$ (British 33).

A complete study of the $UF_{4(s)} + UF_{6(g)}$ reaction was then undertaken at the SAM-Carbide and Carbon Laboratories, and led to the discovery that under appropriate conditions the reaction of UF_4 with UF_6 gas can give rise to α or β forms of UF_5, U_2F_9, or U_4F_{17}. The composition of the compound U_2F_9 and U_4F_{17} was established by chemical analysis. For reference the calculated values of total U, U(IV), and F for various uranium fluorides have been collected in Table 9.

The total uranium and fluorine contents are relatively insensitive to changes in composition between UF_4 and UF_5. The content of tetravalent uranium is therefore a much more satisfactory index of composition (Table 9). In Table 10 (SAM-Carbide and Carbon 3) are given the results of a number of analyses of "black fluoride."

TABLE 9

COMPOSITION OF VARIOUS FLUORIDES

Compound	Per Cent Total U	Per Cent U(IV)	Per Cent F	F/U	$\frac{U(IV)}{U} \times 100$
UF_4	75.8	75.8	24.2	4.00	100.0
U_4F_{17}	74.7	65.4	25.3	4.25	87.5
U_2F_9	73.6	55.2	26.4	4.50	75.0
UF_5	71.5	35.8	28.5	5.00	50.0
UF_6	67.7	0.0	32.3	6.00	0.0

TABLE 10

COMPOSITION OF "BLACK FLUORIDE"; U_2F_9

Sample	Per Cent U	Per Cent U(IV)	Per Cent F	F/U*
I	72.8	54.0	25.6	4.41
II	72.8	53.3	27.1	4.67
III	72.1	52.0	26.4	4.59

*Excellent agreement was obtained by comparing the chemical ratio, F/U with the ratio calculated by weight loss (by escape of UF_6) on heating at 340°C for twenty-four hours at 10^{-5} mm Hg pressure. The weight loss was 4.39 percent.

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Analyses of a number of samples of the substance designated as U_4F_{17} (first detected by x-ray methods) showed that this composition agrees best with the analytic data (Table 11) (SAM-Carbide and Carbon 4).

TABLE 11

COMPOSITION OF U_4F_{17}($UF_{4.25}$)

Composition Per Cent	From Weight Gain *	From Chemical Analysis	Calculated Composition		
			$UF_{4.20}$	$UF_{4.25}$	$UF_{4.30}$
Total U	74.8	74.8	74.9	74.7	74.5
U(IV)	65.7	64.1±1.1 **	67.4	65.4	63.4
F	25.2	25.3±0.2 ***	25.1	25.3	25.5

*From gain in weight when solid UF_4 is treated with gaseous UF_6 at 17 mm Hg pressure (300°C).

**Mean of 6 determinations.

***Mean of 2 determinations.

That samples of U_2F_9 prepared in different ways have an identical lattice constant as indicated by precision x-ray studies is strong evidence for the existence of a true compound of this composition. The existence of U_4F_{17} as a pure compound is not quite as definite, but there is little reason to doubt it.

3.2 Preparation. The UF_4-UF_6 Reaction. The reaction of gaseous UF_6 with UF_4 proceeds in stepwise fashion and can yield U_4F_{17}, U_2F_9, α-UF_5 or β-UF_5 depending on the temperature and the partial pressure of the UF_6 in the system. In Table 12 and Figure 3 are summarized equilibrium conditions for the formation of the various products.

The rate at which equilibrium is attained (and consequently the purity of the product under any given set of conditions) is primarily dependent on the nature of the UF_4 . UF_4 prepared from aqueous solution and then dehydrated has a surface area of 6-8 m^2/g as compared to 0.25 m^2/g for material prepared by high temperature hydrofluorination. The high surface material is to be preferred for rapid attainment of equilibrium. The rate is also strongly affected by sintering which is observed at temperatures above 200°C when either UF_5 or U_2F_9 are the stable phases.

The reaction of <u>liquid</u> UF_6 with UF_4 has not been studied in detail. The product at 100°-125°C is β-UF_5 provided large surface UF_4 is used. With low area UF_4, or when insufficient time for the attainment of equilibrium is permitted, U_2F_9 is the product. This difference in the reactivity of the UF_4 appears to be responsible for the original discovery of the black fluoride. With large surface UF_4 and reaction periods up to one week the reaction of UF_4 with liquid UF_6 at 125°C affords a good method for the preparation of β-UF_5. In general, however, the reactions with gaseous UF_6 are to be preferred, at least pending more detailed information on the liquid phase reactions.

The original method of Ruff and Heinzelmann (1911) for the preparation of UF_5 has been reinvestigated by the Brown University group (Brown 4,7,9). Uranium pentachloride is treated with excess liquid hydrogen fluoride for twelve hours at room temperature in either a nickel or a platinum vessel after which the excess hydrogen fluoride and hydrogen chloride are removed in a stream of nitrogen. The UF_5 produced is the β-form. Uranium hexachloride may also be used. In this case the reaction proceeds as follows:

(50) $$2UCl_6 + 10HF \longrightarrow 2UF_5 + 10\ HCl + Cl_2$$

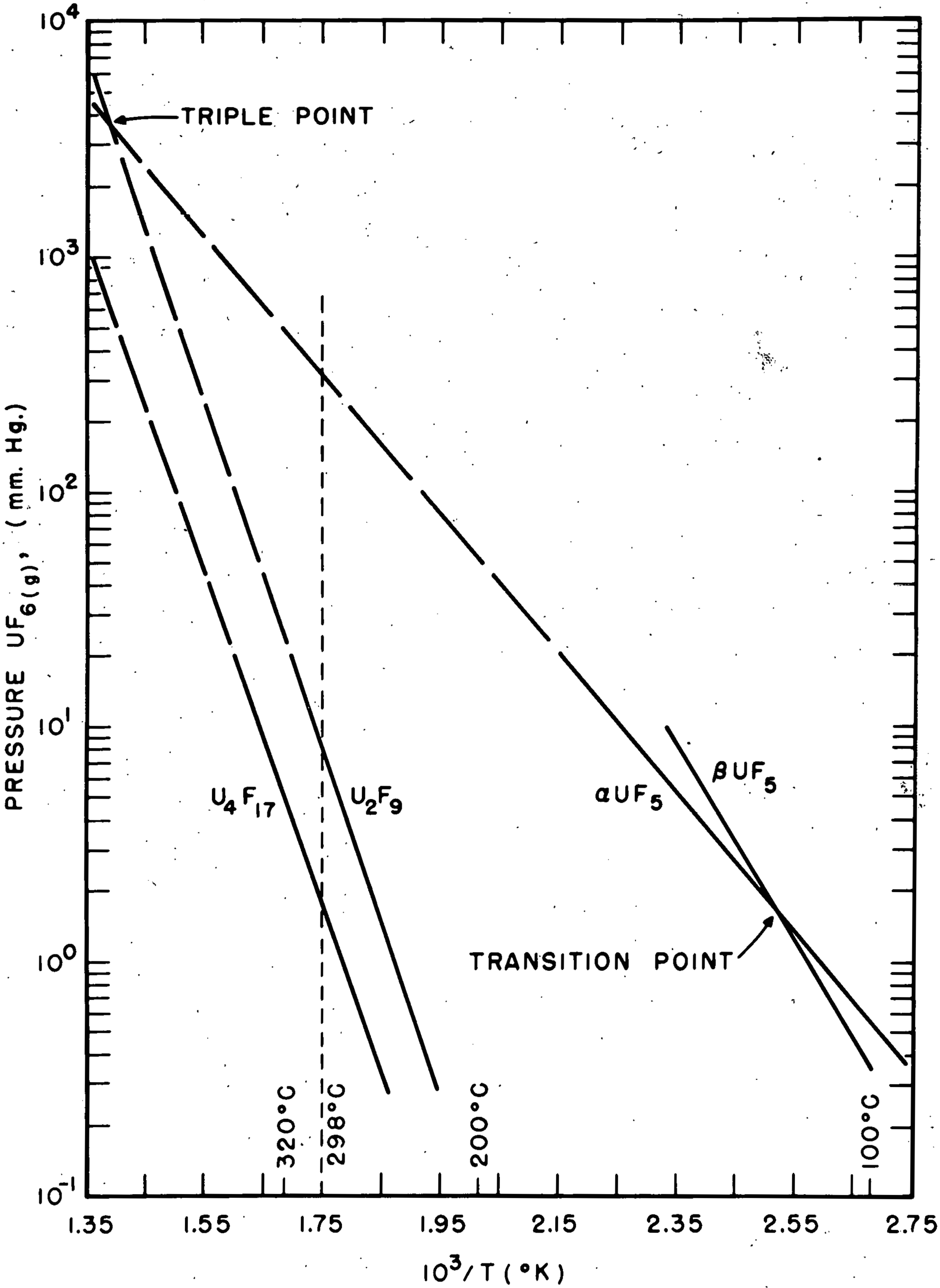

FIG. 3. DISPROPORTIONATION PRESSURES OF U_4F_{17}, U_2F_9, αUF_5 AND βUF_5.

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PHASE RELATIONSHIPS IN THE NaF-UF_4 SYSTEM

Mole Per Cent UF_4		Phases Present
67		UF_4 + $NaUF_5$
50		$NaUF_5$
40	a.	αNa_2UF_6 + trace $NaUF_5$
	b.	αNa_2UF_6
36		αNa_2UF_6
33	a.	αNa_2UF_6 + γNa_2UF_6
	b.	γNa_2UF_6
	c.	βNa_2UF_6 + γNa_2UF_6
31		γNa_2UF_6
29		Na_3UF_7
27		Na_3UF_7
25		Na_3UF_7
20		Na_3UF_7 + NaF

$Na_{4-x}U_xF_{4+3x}$, where x can have values between 1.33 (corresponding to Na_2UF_6) and 1.60.

The phase is cubic face-centered. The lattice constants vary with the value of x:

x	a	ρ (g/cc)
1.33	5.565±0.005 A	5.08
1.45	5.57[illegible]±0.005	5.35
1.60	5.602±0.001	5.66

TABLE 12

CONDITIONS FOR THE PREPARATION OF UF_5 AND THE INTERMEDIATE FLUORIDES BY REACTION OF SOLID UF_4 WITH GASEOUS UF_6

P_{UF_6} (mm Hg)*	100°C	200°C	320°C
17.7	---**	U_2F_9	U_4F_{17}
120-140	β-UF_5	α-UF_5	U_2F_9

* The two pressures given correspond to the vapor pressure of solid UF_6 at 0°C and room temperature respectively.
** Presumably β-UF_5 would be formed under these conditions.

The UCl_6 must be very carefully purified from organic matter (by sublimation) and the hydrogen fluoride free of all traces of moisture (by pretreatment with UCl_5) to obtain UF_5 free of UF_4. Action of gaseous hydrogen fluoride at 300°C on UCl_5 is another effective method for preparing α-UF_5.

Uranium pentafluoride may also be prepared by the reaction of uranium tetrafluoride with fluorine:

$$(51) \qquad UF_4 + F_2 \xrightarrow{150\text{-}250^\circ C} UF_5$$

At higher temperatures ($\sim$370°C) UF_6 is the principal product, but at temperatures of 150-250°C, α-UF_5 of quite high purity can be obtained especially if large-surface UF_4 is employed. The conversion of UF_4 to UF_5 has been accomplished at temperatures below 100°C by using fluorine under pressure (100 lb/in^2) (SAM-Columbia 8). This reaction has not been thoroughly studied; occasionally it, too, gives dark-colored products. The reaction can then be completed by mild treatment in a fluorine stream.

3.3 Disproportionation of UF_5 and the Intermediate Fluorides (SAM-Carbide and Carbon 5). The disproportionation pressures of gaseous UF_6 over α and β-UF_5, U_2F_9 and U_4F_{17} have been measured at SAM-Carbide and Carbon. The results are summarized in Table 13 and Fig. 3.

3.4 Thermochemistry of the Intermediate Fluorides (SAM-Carbide and Carbon 5). From the data in Tables 13 and 14 the thermodynamic functions of the intermediate fluorides may be computed (Table 15).

The heat capacity of (α) UF_5 has been measured at the National Bureau of Standards. The sample contained only 82.82 per cent UF_5, and consequently the results are not very precise. The value of S_{298} obtained from the heat capacity measurements (45 ± 3 e.u) falls between the values calculated above for α - and β - UF_5. The heat capacity measurements are summarized in Table 16.

3.5 Physical Properties and Crystal Structures of the Intermediate Fluorides. Pure UF_5, either α or β, is probably colorless since samples have been prepared which are almost white. However, material within analytical limits for UF_5 has been prepared which is green ($UF_4 + UF_{6(g)}$), pale grey ($UF_4 + F_2$), or even brown ($HF + UCl_5$). All of these variously colored samples give x-ray patterns showing only UF_5. Both U_2F_9 and U_4F_{17} are black. As in the case of U_3O_8, the black color of these compounds is possibly due to resonance in the crystal between uranium ions in different valence states.

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TABLE 13

EQUILIBRIUM DECOMPOSITION PRESSURES AND THERMODYNAMICS OF DISPROPORTIONATION REACTIONS

Reaction	Equilibrium Vapor Pressures $\log_{10} P_{mm} = -\frac{A}{T} + B$		Temperature Range (°C)	Thermochemical Constants		
	A	B		ΔH kcal/mole $UF_6(g)$	ΔS (e.u.)	$F^o_{298^o}$ kcal/mole $UF_6(g)$
$3\ \alpha\text{-}UF_5 \rightleftharpoons U_2F_9 + UF_6(g)$	2942	7.634	100-200	13.46±0.2	21.7±0.3	6.99± 0.4
$3\ \beta\text{-}UF_5 \rightleftharpoons U_2F_9 + UF_6(g)$	4166	10.71	100-152	19.06 ± 0.5	35.8 ± 0.7	8.40 ± 0.8
$7/2\ U_2F_9 \rightleftharpoons 3/2\ U_4F_{17} + UF_6(g)$	7315	13.68	225-320	33.47 ± 1	49.4 ± 1.4	18.8 ± 1.7
$2U_4F_{17} \rightleftharpoons 7UF_4 + UF_6(g)$	7143	12.75	270-350	32.68 ± 0.4	45.2 ± 0.6	19.2 ± 0.7

TABLE 14

THERMODYNAMIC FUNCTIONS

Substance	$\Delta H^{o}_{298^{o}}$ (kcal/mole)	$S_{298^{o}}$ (e.u.)	$\Delta F^{o}_{298^{o}}$ (kcal/mole)
$UF_{6(g)}$	-504 ± 3.	90.3±1	483.9 ± 3
UF_4	-443.5 ± 2	36.1 ± 0.1	421.7 ± 2
U		12.0 ± 0.03	
$F_{2(g)}$[*]		48.58± 0.1	

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[*] From K. K. Kelley, Bureau of Mines Bulletin, No. 434 (1941).

TABLE 15

THERMODYNAMIC FUNCTIONS OF THE INTERMEDIATE FLUORIDES

Substance	$\Delta H^{o}_{298^{o}}$ (kcal/mole)	$S_{298^{o}}$ (e.u.)	$\Delta F^{o}_{298^{o}}$ (kcal/mole)
α-UF_5	-483.7 ± 1.3	48.0 ± 0.4	-458.2 ± 1.4
β -UF_5	-485.2 ± 1.4	43.3 ± 0.5	-458.7 ± 1.5
U_2F_9	-933.8 ± 3	75.3 ± 0.6	-884.0 ± 3
U_4F_{17}	-1820.5 ± 4	149.0 ± 0.6	-1727.5 ± 4

TABLE 16

HEAT CAPACITY AND ENTROPY OF UF_5

$T°/K$	C_p	$H-H_o$	$S-S_o$	$(H-H_o) - T(S-S_o)$
0	0	0	0	0
25	4.23	39	2.23	- 17
50	10.24	219	6.99	-130
75	15.43	544	12.18	-370
100	19.11	978	17.16	-737
125	21.79	1490	21.72	-1224
150	23.97	2065	25.89	-1821
175	25.77	2685	29.72	-2516
200	27.30	3349	33.27	-3305
225	28.61	4049	36.56	-4178
250	29.71	4778	39.63	-5131
275	30.74	5534	42.52	-6158
300	31.69	6314	45.23	-7255
310	32.04	6633	46.28	-7713

(a) Structure of α-UF_5 (MP Chicago 17). α-Uranium pentafluoride exhibits tetragonal symmetry with lattice constants:

$a_1 = 6.512 \pm 0.001$ A $\quad\quad a_3 = 4.463 \pm 0.001$ A

There are two molecules per unit cell, and the calculated density is 5.81 g/cc. Although the full structure is not deducible from the powder diagrams, it has been suggested that the two uranium atoms in the unit cell are at positions (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and that two of the ten fluorine atoms are at $(0,0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},0)$. An idealized structure can be devised corresponding to a close-packing (in the a_1 and a_3 directions) of chains extending indefinitely in the a_3 direction, each chain consisting of UF_6 octahedra in which each octahedron shares two, and only two, opposite corners with adjacent octahedra.

(b) Structure of β-UF_5. β-UF_5 possesses a tetragonal, body-centered structure with the parameters:

$a_1 = 11.450 \pm 0.002$ Å $\qquad a_3 = 5.198 \pm 0.001$ Å

There are eight molecules per unit cell, and the calculated density is 6.45 g/cc (approximately 10 per cent greater than α-UF_5). The eight uranium atoms occupy positions $(0,0,0)\ (\frac{1}{2},\frac{1}{2},\frac{1}{2}) + (x,\frac{1}{4},1/8)\ (\bar{x}, 3/4\ 1/8)\ (3/4, x, 7/8)\ (\frac{1}{4}, \bar{x}, 7/8)$, space group $I\bar{4}2d$. A reasonable allocation of the fluorine atoms is:

$8\,F_I$ in $(x,\frac{1}{4}, 1/8)\ (\bar{x}, 3/4, 1/8)\ (3/4, x, 7/8)\ (\frac{1}{4},\bar{x}, 7/8)$; $x = 0.278$

$16F_{II} + 16F_{III}$ in $(xyz)\ (\bar{x}\bar{y}z)\ (\bar{x}, \frac{1}{2}+y, \frac{1}{4}-z)\ (x,\frac{1}{2}-y,\frac{1}{4}-z)\ (\bar{y}x\bar{z})\ (y\bar{x}\bar{z})$

$(\bar{y}, \frac{1}{2}-x, \frac{1}{4}+z)\ (y,\frac{1}{2}+x, \frac{1}{4}+z)$

with parameters:

	x	y	z
F_{II}	0.167	0.083	0
F_{III}	0.042	0.125	0.443

Each uranium atom is thus bonded to seven fluorine atoms with U-F = 2.23 Å. Four of the seven corners in each fluorine polyhedron about a uranium atom are shared with adjacent polyhedra.

(c) Interconversion of α- and β-UF_5. From the equilibrium pressure equations of α-and β-UF_5, a transition temperature of 125°C (under 1.76 mm UF_6 pressure) is calculated, with α - UF_5 the stable form above 125°C. To effect complete conversion of the β- form, twelve hours at 185°C may be required since at lower temperatures the rate is very slow. The reverse transformation, α into β, has not as yet been achieved.

(d) Structure of U_2F_9 (M P Chicago 18). This crystal has a cubic structure with $a_o = 8.4538_4 \pm 0.001_5$ Å The unit cell contains eight molecules with a calculated density of 7.06 g/cc. A structure with the symmetry $I\bar{4}3m$ has been suggested with atom positions (using the notation of the "International Tables for the Determination of Crystal Structure," Chemical Catalog Company, New York, 1935):

8 U in positions (a) with $x = 0.187 \pm 0.004$
12 F_1 in positions (e) with $x = 0.225$
24 F_{11} in positions (g) with $x = 0.20$, $z = 0.46$

In this structure each uranium is bound to nine fluorine atoms while each fluorine atom is linked to two uranium atoms. The three nearest F_I atoms about each uranium atom are at a distance $U\text{-}F_I = 2.26$ Å; three of the six F_{II} atoms are at a distance of $U\text{-}F_{II} = 2.31$ Å and three others at 2.34 Å. By trivial changes in the fluorine parameters the three distances can be made equal. Since each fluorine atom is bound to two uranium atoms, U_2F_9 should be much less volatile than UF_6 or UF_5 in which all or some of the fluorine atoms are bound directly to only one urenium atom. The volatility of U_2F_9 is comparable to that of UF_4.

The uranium atoms are all structurally equivalent. The formulae $UF_4 \cdot UF_5$ or $3UF_4 \cdot UF_6$ which indicate the presence of two kinds of uranium atoms are therefore inadmissible. The substance may be regarded as a mixed crystal with rational proportions in which resonance renders all of the uranium atoms equivalent:

$$(U^{+4}_{0.5} + U^{+5}_{0.5})\ F_{4.5} \text{ or } (U^{+4}_{0.75} + U^{+6}_{0.25})\ F_{4.5}$$

(e) Structure of U_4F_{17}. (SAM-Carbide and Carbon 4). The crystal structure of this compound has not yet been worked out. The diffraction pattern resembles that of UF_4 in a general way, but differs sufficiently in detail to be designated as "distorted UF_4", and to be considered as belonging to a definite compound. The density of U_4F_{17} (by liquid displacement) is 6.94 g/cc.

(f) Melting Point and Volatility of Uranium Pentafluoride. The melting point of UF_5, although not yet determined with precision, is estimated to lie below 400°C. There is also some evidence for the vaporization of UF_5 without chemical change, but the data are fragmentary, and no definite value for the vapor pressure of UF_5 can be given.

3.6 Chemical Properties. Apart from thermal disproportionation which has already been discussed above, little can be said about the chemical reactions of the intermediate fluorides. All of these compounds undergo hydrolysis. UF_5 resembles UF_6 in its sensitivity to traces of moisture. In moist air α-UF_5 appears to be more susceptible to hydrolysis than β-UF_5, a behavior which is independent of particle size. With water uranyl fluoride and UF_4 are formed:

$$(52)\qquad 2UF_5 + 2H_2O \longrightarrow \underline{UF_4} + UO_2^{++} + 2F^- + 4HF$$

U_2F_9 appears to be much more stable to hydrolysis than UF_5. In water the black color of the compound may persist for an hour or more; in air a sample may remain black for two weeks.

U_4F_{17} reacts with water, but no rate comparison with the other intermediate fluorides are available. Presumably it would be less reactive than U_2F_9. The reaction with water proceeds as follows:

(53) $$2U_4F_{17} + 2H_2O \longrightarrow UO_2^{++} + 7UF_4 + 4HF + 2F^-$$

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CHAPTER 13

URANIUM HEXAFLUORIDE

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URANIUM HEXAFLUORIDE UF_6

Uranium hexafluoride was discovered by O. Ruff and A. Heinzelmann (1909) . Earlier, H. Moissan (1900) had observed that fluorine reacted vigorously with uranium to give a volatile uranium compound; the quantity obtained, however, was too small for study. Ruff, who had previously studied the volatile heavy metal fluorides, MoF_6 and WF_6 (Ruff 1909), suspected the existence of an analogous compound of uranium, and succeeded in preparing it by the reaction of fluorine with uranium metal, uranium carbide or uranium pentafluoride. He determined some of the physical and chemical properties of UF_6 (Ruff, 1911), but recent work has necessitated revision of some of his early results.

For thirty years after Ruff's investigation, uranium hexafluoride received but little attention, and the few recorded preparations were all according to his method. A. V. Grosse (1932) prepared a small quantity for Aston's mass spectrographic study of the uranium isotopes (Aston, 1931), and small amounts also were made for various magnetic and electron diffraction studies. The discovery of uranium fission in 1939 naturally directed new attention to UF_6 as the only known stable gaseous compound of uranium. Much progress has since been made in the search for new preparative methods suitable for laboratory and industry, in the development of methods of handling uranium hexafluoride, and in the determination of the physical properties of this compound. The chemistry of uranium hexafluoride has not been investigated with the same vigor, and much of chemical interest still remains to be done.

1. Preparation of Uranium Hexafluoride

There are two general methods of preparing uranium hexafluoride, one necessitating, either directly or indirectly, the use of elemental fluorine, the other depending on disproportionation reactions. Preparations of the first class are based on the observation that all compounds of uranium yield UF_6 when treated with fluorine under appropriate conditions. Among methods of this type, the most useful in both the laboratory or on an industrial scale are those requiring the least amount of fluorine. Preparations of the second class have as yet received little study, but do offer considerable promise for the future.

1.1 Fluorination of Uranium Compounds. O. Ruff and A. Heinzelmann (1911) first prepared uranium hexafluoride by the action of fluorine on uranium metal or carbide:

(1) $$U + 3F_2 \longrightarrow UF_6$$

(ΔH = -505 - 3kcal/mole) (See Sec. 2.2a)

(2) $$UC_2 + 7F_2 \longrightarrow UF_6 + 2CF_4$$

Reaction (1) proceeds very vigorously with evolution of considerable heat.

Heating is usually required to start the reaction unless the metal is finely divided, but once the reaction has been initiated, it progresses as rapidly as fluorine is admitted to the system. Ruff claimed that gaseous chlorine was required as a catalyst for this reaction, and introduced chlorine or calcium chloride into the reactor. This procedure was followed by several later investigators (e.g., Grosse, Henkel, and Klemm). Recent work, however, has proved that chlorine or other catalysts are not necessary, (MP Chicago 1; British 1), and that the presence of chlorine leads to an impure yellow product instead of pure white uranium hexafluoride. Reaction (2) is less vigorous than (1), but requires much more fluorine. A temperature of 350°C is suitable for reaction (2).

Ruff and Heinzelmann also used the reaction of fluorine with uranium pentachloride at -40°C to prepare uranium hexafluoride. They formulated this reaction as follows:

$$(3) \qquad 2UCl_5 + 5F_2 \longrightarrow UF_4 + UF_6 + 5Cl_2$$

However, the exact composition of the reaction products has not been determined. The possible formation of explosive chlorine fluorides is a hazard. Intense cooling is required, and the UF_6 is separated by distillation after the completion of the reaction. Other uranium halides can be converted to UF_6 in a similar way. On the other hand, Ruff and Heinzelmann were unable to convert a suspension of UCl_5 in liquid chlorine to UF_6 with free fluorine. They concluded that either the rate of the reaction is very slow at the temperatures of liquid chlorine (-33.7°C), or that fluorine must be practically insoluble in liquid chlorine.

The fluorination method of uranium hexafluoride preparation was substantially improved by P. Abelson at the National Bureau of Standards (1), who introduced the use of uranium tetrafluoride instead of uranium metal:

$$(4)\qquad UF_4 + F_2 \longrightarrow UF_6$$

Abelson recommended a temperature of 275°C for this reaction, and used fused sodium chloride as a catalyst. British workers, however, found that sodium chloride or any other catalyst is unnecessary and even detrimental to sucessful fluorination (British 1). Pending further study, it may be suggested that the uranium tetrafluoride used in reaction (4) should be as pure as possible.

Uranium tetrafluoride is readily fluorinated at relatively low temperatures. At room temperature, the reaction is slow, but at 250°C it is very rapid. Below 250°C, the reaction appears to occur in two steps:

$$(5)\qquad 2UF_4 + F_2 \longrightarrow 2UF_5$$

$$(6)\qquad 2UF_5 + F_2 \longrightarrow 2UF_6$$

Reaction (5) proceeds much more rapidly than (6), so that little or no UF_6 appears until all of the UF_4 has been converted to UF_5. Reaction (5) is efficent in utilization of fluorine, while reaction (6) has poor efficiency resulting in large amounts of unused fluorine. Increasing the temperature is of little practical value; the rate of reaction (6) appears rather insensitive to temperature variations between 250°C and 650°C. The reason for this peculiar behavior is unknown. One method of increasing the amount of fluorine consumed is to pass the gas from the reactor where reaction (6) takes place through a second reactor where reaction (5) is carried out. The latter will absorb practically all the residual fluorine. The direction of flow can then be reversed. However doubts have been expressed as to the practicability of this procedure, since experiments show that reaction (5) will be finished in the second reactor before reaction (6) is complete in the first one (British 1). The use of a very long reactor has also been attempted, but even so it has not been found possible to utilize more than 60 to 70 per cent of the fluorine. Attempts to utilize more than 80 per cent of the tetrafluoride lead to a great waste of fluorine (Columbia).

At temperatures of 350°-400°C the separation of the fluoration steps (5) and (6) becomes less clear, and the reaction may be considered a one-step process:

$$(4) \qquad UF_4 + F_2 \longrightarrow UF_6$$

About 375°C appears to be the optimum temperature for the fluorination of UF_4.* Particle size is important; if the UF_4 is finely ground, the temperature of reaction can be markedly reduced. In

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* It has been reported that UF_4 can be converted to UF_6 at room temperature by using fluorine under high pressure (300 lb/in^2) (Columbia 2), but no details of this process are available.

carrying out the conversion of small quantities of UF_4 to UF_6 by fluorination, a dry-out period of at least 24 hours (preferably 2 to 3 days) has been recommended (British 2), during which the furnace should be kept at 400°C, and a high vacuum maintained in order to eliminate the last traces of moisture.

Another method of preparation of UF_6, suggested by the Columbia University workers, is as follows (Columbia 3):

(7) $UO_3 + H_2F_2 \xrightarrow{350^{\circ}C} UO_2F_2 + H_2O$

(8) $UO_2F_2 + 2F_2 \longrightarrow UF_6 + O_2$ + oxygen fluoride

Uranyl fluoride can be readily prepared by the action of anhydrous hydrogen fluoride on the trioxide at 350°C. Alternatively, hydrated uranyl fluoride can be made by the action of aqueous hydrofluoric acid (48 per cent) on the trioxide; the hydrated UO_2F_2 can then be completely dehydrated at 300°C. The following fluorination of UO_2F_2 proceeds more smoothly than that of UF_4 at a temperature of 150° to 400°C. Uranium hexafluoride collects within a few minutes after fluorine is admitted to the reactor. The fluorine is almost completely utilized, except for that fraction which forms oxygen fluoride. The principal advantage of this process is the ease of preparation of uranyl fluoride; the principal disadvantage is that it requires twice as much free fluorine per mole of UF_6 as does the fluorination of UF_4.

It appears that all uranium compounds when heated with fluorine to a sufficiently high temperature will give UF_6 (CEW-TEC 1). Uranyl phosphate, for example, readily undergoes conversion to UF_6 and PF_3 or $PF_5 \overset{\text{at}}{/} 400^{\circ}C$. Oxides of uranium are said to require heating with fluorine to a temperature of 400°-500°C, and to be, in general rather difficult to fluorinat

However, uranium sesquioxide can be converted to UF_6 at 300°C if carbon is added to the mixture (MP Chicago 1):

(9) $U_3O_8 + 4C + 9F_6 \rightarrow 3UF_6 + 4CO_2$

According to some reports, pure U_3O_8 reacts with fluorine at 360-370°C (Columbia 4):

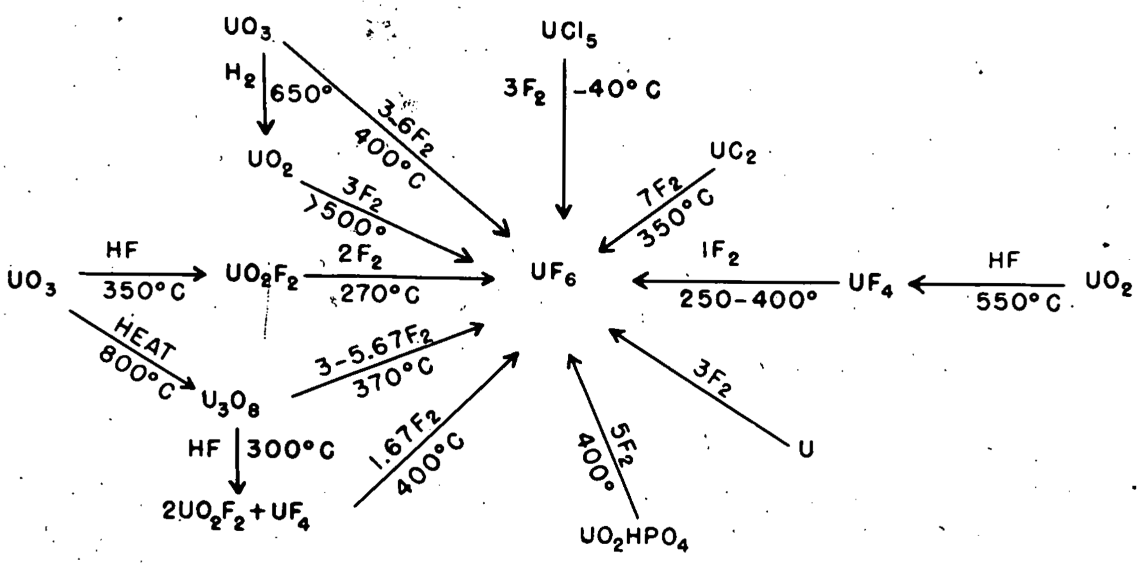
(10) $U_3O_8 + 17F_2 \rightarrow 3UF_6 + 8OF_2$

Another proposed method of converting U_3O_8 to UF_6 involves preliminary hydrofluorination (MP Chicago 1):

(11) $U_3O_8 + 8HF \xrightarrow{500^\circ C} 2UO_2F_2 + UF_4 + 4H_2O$

(12) $UF_4 + 2UO_2F_2 + 5F_2 \longrightarrow 3UF_6 + 2O_2$

The following diagram summarizes the necessary conditions to assure formation of UF_6 from a variety of uranium compounds.



CONVERSION OF URANIUM COMPOUNDS TO UF_6

(SHOWING NUMBER OF MOLES OF F_2 REQUIRED FOR THE FORMATION OF ONE MOLE UF_6).

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Fluorination reactions are best carried out in nickel or monel vessels, although copper, aluminum, and magnesium can also be employed. Platinum cannot be used since it is rapidly attacked by fluorine above 450°C. Calcium fluoride reaction tubes and boats are very useful but are not readily available. Standard flare fittings, such as are used in the refrigeration industry, are convenient for assembling copper apparatus. At low temperatures fluorine can be handled without serious attack for considerable periods in thoroughly dried and outgassed pyrex or quartz vessels. Soft glass is reputed to be superior to pyrex in its resistance to fluorine. Further manipulative details will be found in Section 1.3.

Fluorination of uranium compounds to UF_6 also can be successfully achieved with certain agents other than elemental fluorine (CEW-TEC 2; Columbia 5; Yale 1). These strong fluorinating agents, however, require fluorine for their preparation, and consequently do not dispense altogether with the use of free fluorine. Their use for the synthesis of UF_6 sometimes has additional advantages besides avoiding free fluorine. Thus, uranium tetrafluoride can be converted to UF_6 by reaction with cobaltic fluoride:

$$(13) \quad UF_4 + 2CoF_3 \xrightarrow{250^\circ\text{-}275^\circ C} UF_6 + 2CoF_2$$

The reaction has been used especially for the conversion of small samples of UF_4 (50 mg to 1 g) to UF_6. The reaction mixture is prepared by grinding the tetrafluoride with fivefold excess of cobaltic fluoride in a dry box. The reaction can be carried out in all-glass apparatus with the reaction mixture placed in a platinum boat. A temperature higher than 275°C is to be avoided as CoF_3 may undergo thermal decomposition. Cobaltic fluoride can be prepared in a variety of ways (CEW-TEC 3):

$$(14) \quad CoCl_2 \times 6H_2O \xrightarrow{400^\circ C} CoCl_2 + 6H_2O$$

$$(15) \quad CoCl_2 + 2HF \xrightarrow{250^\circ C} CoF_2 + 2HCl$$

$$(16) \quad 2CoF_2 + F_2 \xrightarrow{250^\circ C} 2CoF_3$$

$$(17) \quad 2CoCl_2 + 5F_2 \xrightarrow{400^\circ C} 2CoF_3 + 4FCl$$

Silver difluoride or palladium trifluoride would probably be as satisfactory as CoF_3. Antimony pentafluoride, on the other hand, a compound which can be prepared without the use of elemental fluorine, does not convert UF_4 to UF_6 (DuPont 1).

1.2 <u>Reactions Not Involving the Use of Elemental Fluorine</u>. Two reactions have been discovered which produce UF_6 without requiring free fluorine. The first is the thermal disproportionation of UF_5:

$$(18) \quad 3UF_5 \xrightarrow{175^\circ C} U_2F_9 + UF_6$$

$$(19) \quad 2U_2F_9 \xrightarrow{>200^\circ C\ (?)} 3UF_4 + UF_6$$

Uranium pentafluoride for reaction (18) can be prepared from the readily available pentachloride:

$$(20) \quad UCl_5 + 5HF \longrightarrow UF_5 + 5HCl$$

Ruff and Heinzelmann (1911), who first used this procedure, experienced considerable difficulty in separating the UF_6 from hydrogen fluoride formed from the compound $UF_5 \cdot HF$ which they used. Subsequent work has indicated that UF_6 can be separated from hydrogen fluoride by fractional distillation, or even more simply, by decantation, since UF_6 is only sparingly soluble in liquid anhydrous hydrogen fluoride at low temperatures (Columbia 6; SAM-Carbon and Carbide 1). The disadvantage of this process is that only one-third of the uranium is utilized and the remainder must be re-worked.

The second method is based on a very interesting reaction recently discovered at Chicago (MP Chicago 2). When uranium tetrafluoride is treated with dry oxygen at elevated temperature (ca. 800°C), the following reaction occurs:*

$$(21) \qquad 2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$$

At Chicago, reaction (21) was carried out in a nickel tube. (Calcium fluoride, being more inert, may be even better.) At 800°C, a yield of 20 to 40 per cent of the calculated amount of UF_6 was obtained. The comparatively low yield is probably due to reaction of UF_6 with nickel. Reaction (21) provides a convenient method for laboratory preparation of UF_6 when no fluorine is available.

Attempts were made by Ergen (SAM-Carbon and Carbide 1) to prepare UF_6 by reactions avoiding free fluorine. Mercuric fluoride was examined as a fluorinating agent. UF_4 and UCl_5 were made to react with HgF_2, or with Hg_2F_2 and chlorine, and in both cases UF_6 was obtained in small quantity.** Uranium pentachloride reacts

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* A similar experiment had been carried out earlier by workers at Brown University in a "Vycor" tube. They observed the formation of a heavy brown deposit and noticed the weight loss of the residue. The possibility that F_2 or UF_6 might be formed was suggested, but no further work appears to have been done at that time (Brown 1).

** The mercuric fluoride, HgF_2, was prepared by reaction of mercurous fluoride (Henne, 1938) with chlorine according to the method of Ruff and Bahlau (1919).

with HgF_2 at "moderate" temperatures to give a white sublimate, presumably UF_6. An intimate mixture of mercurous fluoride and UF_4, when treated with dry chlorine at 400°C in a glass apparatus yielded a small quantity of UF_6. The low yield was attributed to side reactions with the glass. An attempt was also made to obtain UF_6 by passing a mixture of chlorine and dichlorodifluormethane over a mixture of UO_3 and mercurous fluoride, but the UO_3 was apparently unattacked.

It is clear from these observations that the preparation of UF_6 without the use of free fluorine is quite feasible.

1.3 Purification and Handling of Uranium Hexafluoride. Since UF_6 is a very reactive substance, handling problems are encountered in both laboratory and large scale use. Usually metal apparatus is employed, but glass may be used successfully if certain precautions are taken. UF_6 attacks glass quite rapidly unless it is absolutely free from water or hydrogen fluoride. Phosphorus pentoxide has been used to dry UF_6, but this is a troublesome procedure (Grosse, 1932). The attack on glass is probably due to the following cycle:

$$(22) \quad UF_6 + 2H_2O \longrightarrow UO_2F_2 + 4HF$$

$$(23) \quad SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

The water consumed in reaction (22) is regenerated in reaction (23), and therefore traces of moisture are capable of destroying large amounts of UF_6. The use of "getters" to stop this cycle was introduced by Grosse (Columbia 6). Sodium or potassium fluoride will combine with all the components of reaction cycle (22) and (23) (giving $KF \cdot HF$, $KF \cdot 2H_2O$, K_2SiF_6 etc.) and thereby stop the cycle. Pure UF_6 does not form a stable addition compound with KF, but UF_6, HF and KF give stable triple compounds. However, the amount of UF_6 lost in this way corresponds only to the stoichiometric quantity of hydrogen fluoride present, which will in most cases be small. Therefore, in order to keep UF_6 in glass, it is only necessary to have present some dry powdered potassium or sodium fluoride amounting to about 5 per cent by weight of the UF_6 (See page). Since potassium fluoride is very hygroscopic, it should be fused before use; sodium fluoride is not deliquescent and may therefore be preferable to potassium fluoride (British 3). It has been reported that pure UF_6 can be kept indefinitely without decomposition, even in the absence of a "getter", in a glass container which has been vacuum baked. The UF_6 must first be purified by multiple vacuum distillation through a train of U-tubes containing potassium fluoride (Columbia 7).

Care must be taken in condensing UF_6 in glass apparatus. Traps cooled with liquid air are inadvisable since they often crack when warmed. To prevent such breakage one should first cool with dry ice so that the material deposits as a fluffy snow. If liquid air is to be used, a trap with an internal cold finger is recommended (Columbia 8).

The following sequence of operations has been found to give clean glass resistant to the action of pure UF_6 (British 4):

1. Washing with xylene or trichloroethylene.
2. Flaming.
3. Pretreating for a few hours with UF_6 vapors at room temperature.

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The most important step in this sequence is pretreatment with UF_6 vapor, which appears to be much more effective than flaming. Since all-glass apparatus is necessary for complete baking out, stopcocks and joints should be avoided by the use of magnetic breaker seals (referred to by British authors as "Briscoe seals"). If glass stopcocks and ground glass joints are used, Apiezon grease or wax, or preferably fluorinated hydrocarbons, may be used for lubrication, but too much of the lubricant must not be exposed to the UF_6.

Because UF_6 sublimes under ordinary conditions and can be distilled as a liquid only under pressure, certain specialized transfer techniques are necessary (Columbia 8). The most generally satisfactory procedure is to put the whole system in an oven heated to 75°C. It is best to handle UF_6 in wide tubing and to use valves with wide openings for metal systems. Any narrow opening may lead to difficulties, since expansion of the vapor may cool it sufficiently to cause condensation. Gases non-condensable by liquid nitrogen must be absent from the system, since they are swept along by the dense UF_6 vapors and accumulate in the condenser where they may completely block further transfer. A vacuum-tight system carefully evacuated in advance must therefore be used for transferring and handling UF_6.

Satisfactory materials for metal equipment are copper, nickel and aluminum. With copper tubing, ordinary refrigeration flare fittings are used for making connections; properly made, such joints are vacuum tight. Kerotest valves are satisfactory for general use. Pressure gauges should be of the Bourdon type, with tubes made of a UF_6-resistant metal. Further details of resistant metals will be found in Section 3.3.

The most common contaminents present in ordinary UF_6 seem to be hydrogen fluoride and volatile MoF_6 which probably arises from stainless steel equipment. Other volatile metal fluorides may also be present. To eliminate hydrogen fluoride, it has been recommended that liquid UF_6 be heated with fused potassium fluoride at 75°C for 48 hours, but some workers have considered treatment at room temperature adequate. For large amounts of UF_6, heating probably is advisable (Columbia 9). Very pure UF_6 has been prepared by fractional distillation in an all-nickel column packed with nickel helices (55 in) (Columbia 10). Distillation takes place above the triple point (64°C and 1334 mm Hg), and reflux is controlled by a condenser containing boiling methyl alcohol (67°C). The entire assembly is placed in a box heated to 75°C to prevent condensation of UF_6. The material obtained from the distillation column is spectroscopically pure, and neither molybdenum nor hydrogen fluoride are detectable.

British workers likewise have found hydrogen fluoride to be the principal impurity in UF_6 (British 5). They recommend much larger quantities of potassium fluoride for the removal of HF, considering about 50 per cent of the weight of UF_6 necessary to remove 2 mole per cent HF. These observers found that a constant evaporation mixture of UF_6 and hydrogen fluoride exists (vapor pressure of 17.91 mm Hg at 0°C), and that the hydrogen fluoride content of an impure UF_6 sample can be reduced to the composition of this mixture (about 2 mole percent HF) by pumping at -80°C. This indicates that potassium fluoride purification should not be applied directly to mixtures with a hydrogen fluoride content greater than 2 mole per cent, until the mixtures have been treated by pumping at -80°C.

The presence and amount of hydrogen fluoride in UF_6 can be determined by either vapor pressure or freezing point measurements. Since hydrogen fluoride is only slightly soluble in UF_6, the vapor pressures are additive. The presence of one mole per cent hydrogen fluoride at 0°C contributes 12.0 mm to the vapor pressure (Columbia 11). To detect very small amounts of hydrogen fluoride the freezing point depression method is more accurate. The experimentally determined cryoscopic constant of UF_6 is 0.065°C per 0.01 weight per cent of hydrogen fluoride. The theoretical value, computed from Raoult's law is 0.0839°C (Columbia 12).

British workers re-examined various methods proposed for the determination of hydrogen fluoride in UF_6. They concluded that the most satisfactory method is one in which the uranium hexafluoride -hydrogen fluoride mixture is refluxed under such conditions that the hydrogen fluoride remains in the vapor phase. The equilibrium volume can be measured to within 0.01 mole per cent of hydrogen fluoride (British 6). For further details on the hydrogen fluoride -uranium hexafluoride system see Section 3.2 of this chapter.

2. **Physical Properties of Uranium Hexafluoride** At room temperature, uranium hexafluoride is a colorless, volatile solid which forms transparent crystals of high refractive index. These crystals sublime without melting under atmospheric pressure; at higher pressures, they melt to form a clear, colorless, mobile liquid of high density. Despite the high molecular weight of UF_6, the properties of its vapor closely approximate those of an ideal gas.

The physical properties of UF_6 in its various states will be considered under the following headings:

Phase Relationships: Melting point, vapor pressure of solid and liquid, boiling point, triple point, and critical constants.

Thermal Properties: Specific heat, entropy and enthalpy, velocity of sound, heats of sublimation, evaporation and fusion, and thermal conductivity.

Mechanical Properties: Density, kinetic properties of the vapor, viscosity, and surface tension.

Optical Properties: Refractive index, absorption spectrum, and Raman spectrum.

Electrical and Magnetic Properties: Dielectric constant, magnetic susceptibility, and ionization potential.

Structure of the Molecule: Derived from electron diffraction, x-ray crystallography and dipole moment measurement.

The graphs included in this chapter are taken from the summary report of I. Kirshenbaum (Columbia 13), which was extensively used by the writers.

2.1 Phase Relationships.

(a) Melting Point. The earliest value of the melting point (69.2-69.5°C), given by Ruff and Heinzelmann (1911), and quoted by A. V. Grosse (Columbia 6), has since been shown to be considerably in error. Brichwedde, Hoge and Scott (Nat. Bur. Standards 2) found a value of 64.052°C (337.212°K) for material containing 2×10^{-2} mole per cent impurities, while British workers gave 64.5 ± 0.3°C and 64.8 ± 0.4°C for two samples containing less than 1.5×10^{-2} per cent of impurity (British 7). From the knowledge of the specific volumes of the liquid and of the solid, V_L and V_S, at the triple point (See p.   and   ), the change in melting point with pressure can be calculated:

$$(24) \qquad \frac{dT}{dP} = \frac{T(V_L - V_S)}{\Delta H_{fusion}} \approx 0.00505 \quad ^{\circ}C/atm.$$

(b) Vapor Pressure of Solid Uranium Hexafluoride. The early vapor pressure values of Ruff and Heinzelmann (1911) were rather erratic, probably due to contamination by hydrogen fluoride or silicon tetrafluoride. Recently, several vapor pressure determinations have been made by British workers and at Columbia University. On the whole, taking into account the difficulty of the measurements, the results can be said to agree satisfactorily. It is difficult to prepare UF_6 completely free of hydrogen fluoride, and this tends to give too high values for the vapor pressure. There is also the difficulty of assuring complete thermal equilibrium between the thermostat and a loose mass of solid UF_6. Finally, the corrosion of construction materials poses a serious problem. American workers have generally used copper apparatus, whereas the British seem to have preferred glass.

At Columbia University a brass sylphon bellows was used to measure the pressure by a null method (Columbia 14). Pressures above atmospheric were read on a multiple mercury manometer using dibutyl phthalate as piston liquid. The error in reading the manometer was about 2 mm in the higher pressure range, and less than 0.5 mm in the lower range.

Table 1 contains a summary of all the directly measured vapor pressures of solid UF_6.

The following linear relationships between log p and 1/T have been suggested for the representation of the vapor pressure curve over a limited temperature range:

~~(25) $\log p_{mm\ Hg} = 10.76 - \frac{2600}{T}$ (12.5 - 50.2°C)~~ (British 8)

(26) $\log p_{mm\ Hg} = 10.8407 - \frac{2623.3}{T}$ (0 - 63.1°C) (Columbia 14)

(27) $\log p_{mm\ Hg} = 11.19 - \frac{2714}{T}$ (low temperatures) (British 9)

Two more elaborate relationships, intended to represent precisely the vapor pressure curve in a wide temperature region have been derived. The equation,

(28) $\log_{10} P_{mm\ Hg} = -\frac{2751}{T} - 75.0\ e^{-2560/T} - 1.01 \log_{10} T + 13.797,$

represents all British measuremtns in the range 0°-65°C with a precision of ±0.5 per cent (British 10); Columbia measurements agree within 1.5 per cent, but all American points lie a little above the curve defined by equation (28).

TABLE 1

VAPOR PRESSURES OF URANIUM HEXAFLUORIDE

Temp.	Pressure (mm Hg)				Temp.	Pressure (mm Hg)			
(°C)	(a)	(c)	(d)	(e)	(°C)	(b)	(c)	(d)	(e)
-14.2	6.85	—	—	—	30.4		158		—
-12.4	7.80	—	—	—	31.2		—	178.4	—
- 1.5	17.80	—	—	—	32.7		—	199.0	—
0.0	—	—	—	16.9	34.9		—	224.3	—
0.1	20.10	—	—	—	35.3	217.7	—	—	
1.7	23.30	—	—	—	35.5	—	—	—	216.8
3.6	26.60	—	—	—	36.8	—	—	259.5	—
5.5	30.40	—	—	—	38.3	—	—	282.8	—
6.8	32.90	—	—	—	39.7	—	—	310.5	—
8.5	37.00	—	—	—	40.0	—	—	—	295.4
11.3	44.00	—	—	—	40.5	—	—	316.5	—
	(b)	—	—	—	41.7	—	—	348.9	—
12.5	45.5	—	—	—	44.7	—	—	—	—
14.3	52.2	—	—	—	45.0	—	—	—	395.8
14.5	52.7	—	—	—	45.2	—	—	418.8	—
14.7	53.8	—	—	—	47.2	—	—	484.1	—
15.0	54.6	—	—	—	49.6	—	—	549.1	—
17.6	66.3	—	—	—	50.0	—	—	—	522.1
20.4	81.1	—	—	—	50.2	523.0	—	559.2	—
21.0	—	83	—	—	51.6	—	—	605.0	—
21.6	—	—	—	88.3	51.8	—	—	612.5	—
22.7	—	93	—	—	53.9	—	—	685.5	—
24.9	—	108	—	—	55.0	—	—	—	697.2
25.0	—	—	119.5	—	55.7	—	—	751.2	—
25.1	113.9	—	—	—	60.0	—	—	[illegible]	910.0
26.4	—	123	—	—	63.1	—	—	—	1072
28.2	—	138	—	—					
29.0	—	—	153.3	—					
29.5	151.0	—		—					

(a) (British 11).
(b) (British 8).
(c) (British 12).
(d) (British 27). = [illegible]
(e) (Columbia 14).

At Columbia (13) another equation based on all the available data was derived. All experimental points were plotted on large scale and a curve was fitted to these points by a series of analytical and graphical approximations, the higher ones involving the application of heat capacity and enthalpy equations for the solid. The resulting equation is said to represent the experimental results to ±0.5 per cent, and perhaps even better (See Fig. 1):

$$\text{(29a)} \quad \ln P_{\text{mm Hg}} = -132.8690 - \frac{344490}{T^2} + \frac{707.31}{T} + 26.436 \ln T - 0.038674\,T$$

or, in Briggsain logarithms:

$$\text{(29b)} \quad \log_{10} P_{\text{mm Hg}} = -57.7043 - \frac{149610}{T^2} + \frac{307.18}{T} + 26.436 \log_{10} T - 0.016796\,T$$

Vapor pressures of solid UF_6 at low temperatures have been extrapolated by means of the equations (27) and (29), with the results shown in Table 2.

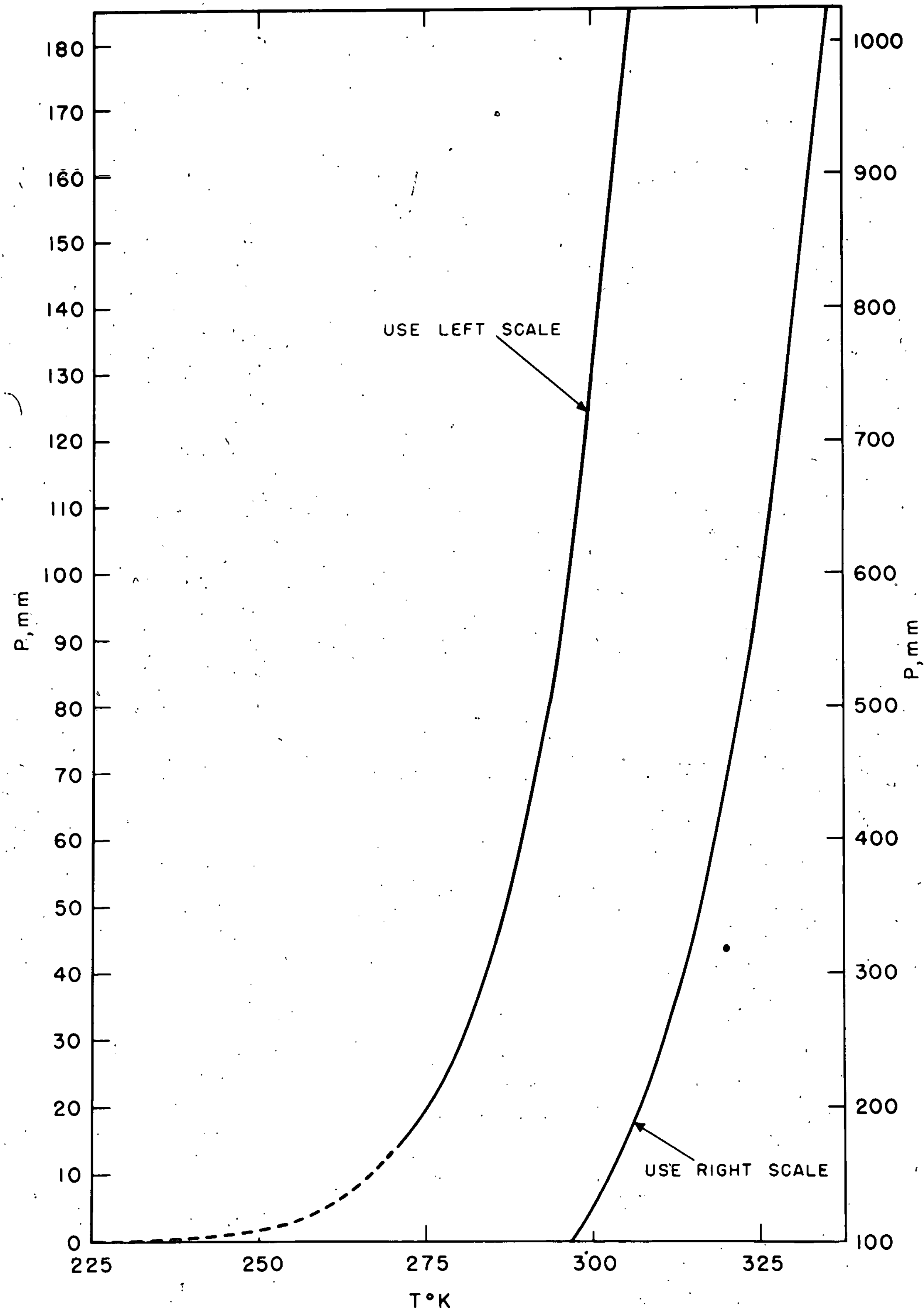

FIG. 1. VAPOR PRESSURE OF $UF_{6(S)}$. (SEE EQUATION 29.)

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TABLE 2

URANIUM HEXAFLUORIDE VAPOR PRESSURE AT LOW TEMPERATURES

Temperature (°C)	Vapor Pressure (mm Hg)	
	(a)	(b)
-200	10^{-26}	--
-183(c)	--	10^{-19}
-150	10^{-11}	--
-103.8(d)	--	1.3×10^{-5}
-100	4.3×10^{-5}	--
-95	8.6×10^{-5}	--
-90	3.0×10^{-4}	--
-85	7.3×10^{-4}	--
-80	1.7×10^{-3}	--
-78.5(e)	--	1.7×10^{-3}
-75	3.8×10^{-3}	--
-70	8.2×10^{-3}	--
-65	1.7×10^{-3}	--
-60	3.4×10^{-2}	--
-55	6.5×10^{-2}	--
-50	1.18×10^{-1}	--
-45	2.2×10^{-1}	--
-40	3.69×10^{-1}	--
-35	6.9×10^{-1}	--
-30	1.16	--
-25	1.92	--
-20	3.11	--

(a) Equation 29 (Columbia 13).
(b) Equation 27 (British 9).
(c) Boiling point of O_2
(d) Boiling point of C_2H_4.
(e) Boiling point of CO_2.

In addition to the value of 16.9 mm quoted in Table 1 several values have been given for the vapor pressure of solid UF_6. At the ice-point (0°C) Columbia workers found a value of 18.0 mm (Columbia 11), while British workers gave as a result of a very careful measurement $P_{mm\ Hg}$ (0°C) = 17.54 ± 0.02 (British 5). The latter value probably is more reliable, since it has been found by British workers that a constant evaporation mixture of UF_6 and HF exists, with a vapor pressure at 0°C of 17.91 ± 0.02 mm.

(c) Vapor Pressure of Liquid Uranium Hexafluoride. Values for the liquid-vapor equilibrium of UF_6 are more accurate than those for the solid-vapor equilibrium, perhaps because of the greater ease with which thermal equilibrium can be achieved. Columbia workers using the same apparatus as for the determination of the solid-vapor equilibrium found the values listed in Table 3 (Columbia 14). The Table also includes results of the British observers (British 5,10).

TABLE 3

VAPOR PRESSURE OF LIQUID URANIUM HEXAFLUORIDE

Temp. (°C)	Pressure			Difference Between Calculated and Observed Values
	(a)	(b)	(c)	
65.0	1175	1169	1170	+1
67.9	--	1273	1277	+4
70.0	1385	--	--	--
70.1	--	1360	1363	3
70.2	--	1366,1370,1376	1367	-1,-3,-9
75.0	1620	--	--	--
75.2	--	1582	1580	-2
75.3	--	1568	1585	+17
80.0	1870	--	--	--
80.3	--	1830,1838	1824	-6,-14
85.0	2165	--	--	--
85.4	--	2087	2098	+11
90.0	2455	--	--	--
95.0	2765	--	--	--

(a) Experimental values (British 5,10).
(b) Experimental values (Columbia 14).
(c) Calculated values (Columbia 14).

The formulae (30 and 31) were given by British observers while formula (32) was derived at Columbia.

$$(30)\quad \log_{10}P_{\text{mm Hg}} = \frac{2170}{T} + 56.0 \log T - 0.0394\, T - 131.64$$

$$(31)\quad \log_{10}P_{\text{mm Hg}} = 7.73 - \frac{1575}{T}$$

$$(32)\quad \log_{10}P_{\text{mm Hg}} = 7.5223 - \frac{1505.9}{T}$$

The last formula was found to reproduce the results to better than ±1 per cent, as shown by figures in the last column of Table 3.

A precision formula for the liquid-gas equilibrium was obtained by Kirschenbaum by the same method as formula (29) for the solid gas equilibrium, that is, by fitting a curve to a large scale plot of the available data by successive approximations: (See Fig. 2).

$$(33a)\quad \ln P_{\text{mm Hg}} = -24.6602 - \frac{248608}{T} - \frac{1245.2}{T} + 7.2876 \ln T - 0.014371\, T$$

or, in Briggsian logarithms

$$(33b)\quad \log_{10}P_{\text{mm Hg}} = -107098 \quad \frac{107969}{T^2} - \frac{540.8}{T} \quad -7.2876 \log_{10} T - 0.006241\, T$$

This equation reproduces the experimental results in the range 65°-90°C to better than -0.4 per cent

(d) Boiling Point. The temperature at which the sublimation pressure of UF_6 reaches 760mm was reported by Ruff and Heinzelmann (1911) as 56°C. More recently Columbia observers found 56.2°C (Columbia 6), and the British investigators 55.3°C and 56.6°C with the higher value considered more nearly correct (British 8). Thus, 56.4°C appears to be a reasonable mean value for the "boiling point" of UF_6. The triple point of UF_6 calculated from equations (29) and (33) is

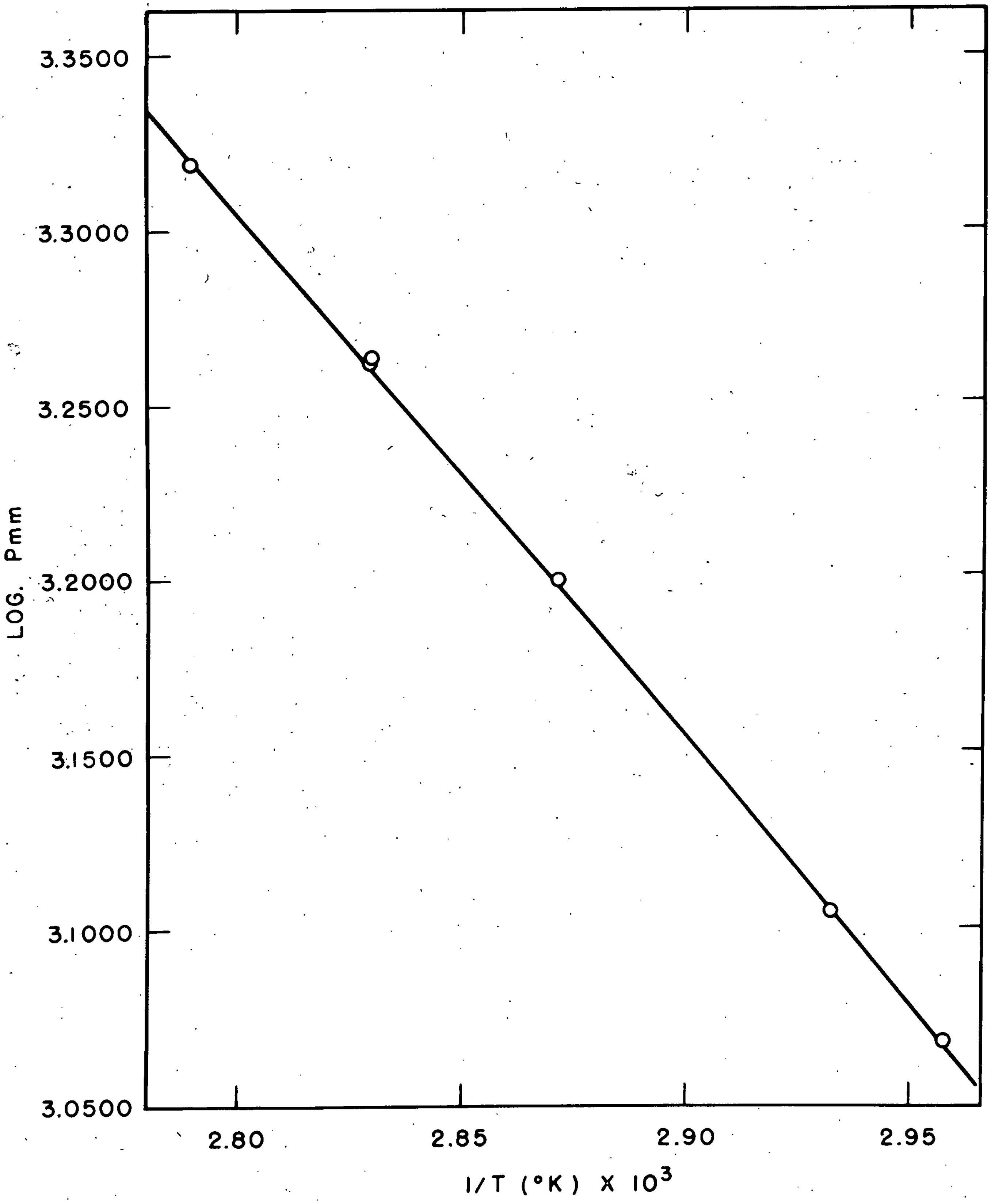

FIG. 2. VAPOR PRESSURE OF $UF_{6(l)}$. (SEE EQUATION 33.)

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(Columbia 14):

$t_{tr.} = 64.052^{\circ}C$

$p_{tr.} = 1134$ mm Hg

(e) Critical Temperature, Pressure, and Density. British workers reported a value of 245 -5°C for the critical temperature of UF_6 (British 14). While Columbia workers found for this constant a value of 232°C (Columbia 13), the National Bureau of Standards (3) estimated from the plot of the densities of the liquid vs. temperature that the critical temperature must be about 217°C. Another approximate value of the critical temperature (243°C) was calculated from the surface tension, γ, by means of the relationship:

$$(34) \quad \gamma = \frac{2.12\,(t_c - 6 - t)}{(MV_L)^{2/3}} \qquad \begin{array}{l} \gamma = 15.6 \text{ dynes at } 80^{\circ}C \\ d = 3.57 \text{ g/cm}^3 \text{ at } 80^{\circ}C \end{array}$$

Finally, from boiling point data and the relationship,

$$\frac{T_b}{T_c} = 0.63,$$

one obtains

$$T_c = 249^{\circ}C$$

British observers estimated the critical pressure as 63 atmospheres (British 15); the Columbia Group as about 50 atmospheres (Columbia 15) and the National Bureau of Standards (3) as 44 atmospheres. The critical density has been estimated at 1.9 g/cc (British 15) and 1.39 g/cc (National Bureau of Standards 3). The latter value is probably more reliable. Obviously, further work on the critical constants is required.

2.2 Thermal Properties

(a) Heat and Free Energy of Formation of Uranium Hexafluoride.

The heat of hydrolysis of UF_6 in water was found calorimetrically to be -50.5 kcal/mole at 298.16°K (Columbia 16).

(35) $UF_{6(c)} + 2H_2O_{(liq)} \longrightarrow UO_2^{++} + 2F^- + 4HF_{aq}$;

$\Delta H = -50.5 \pm 1.7$ kcal/mole

Using the value,

$\Delta H_{subl} = -11.2 \pm 1$ kcal/mole,

for the heat of sublimation of UF_6 (Columbia 14) and combining these results with the following data from the literature;

$UO_2^{++} + 3H_2 \longrightarrow 2H^+ + 2H_2O + U \qquad \Delta H = 106.3$ kcal

$2H^+ + 2F^- \longrightarrow 2HF_{(aq)} \qquad \Delta H = 4.0$ kcal

$6HF_{(aq)} \longrightarrow 3H_{2(g)} + 3F_{2(g)} \qquad \Delta H = 456$ kcal

one finds for the heat of formation of UF_6

(36) $U_{(s)} + 3F_{2(g)} \longrightarrow UF_{6(g)} \qquad \Delta H = -505 \pm 3$ kcal/mole

Using the entropy values $S_{298} = 90.3 \pm 0.1$ e.u. for UF_6 and $S_{298} = 12.0$ e.u. for uranium metal, one calculates for the free energy of formation of UF_6

$$\Delta F_{298} = -485 \text{ kcal/mole.}$$

(b) Heat Capacity, Entropy and Enthalpy of the Solid and Liquid. The heat capacities of solid and liquid UF_6 in equilibrium with the vapor have been very accurately determined at the National Bureau of Standards (2). Entropies and enthalpies calculated from these data are given in Table 4. The values are propably accurate to within ± 1 per cent.

TABLE 4

HEAT CAPACITY, ENTROPY AND ENTHALPY OF URANIUM HEXAFLUORIDE

Temperature (°K)	Cp (cal/mole °K)	$H-H_o$ (cal/mole)	$S-S_o$ (cal/mole °K)	$T(S-S_o)$ (cal/mole)
(Solid)				
0	0	0	0	0
20	4.06	28.0	1.96	39
25	5.53	52.0	3.04	76
30	6.92	83.2	4.16	125
35	8.27	121.1	5.33	187
40	9.64	165.9	6.53	261
45	11.00	217.5	7.72	347
50	12.34	275.9	8.96	448
55	13.66	340.9	10.21	562
60	14.90	412.4	11.45	687
65	16.07	489.8	12.69	825
70	17.16	572.8	13.91	974
75	18.22	661.4	15.13	1135
80	19.20	754.9	16.35	1308
85	20.14	853.9	17.55	1492
90	20.99	956.2	18.72	1685
95	21.76	1063	19.86	1887
100	22.49	1174	20.99	2099
105	23.17	1288	22.11	2322
110	23.82	1405	23.21	2553
115	24.46	1526	24.29	2793
120	25.08	1650	25.34	3041
125	25.66	1777	26.37	3296
130	26.23	1907	27.39	3561
135	26.77	2039	28.40	3834
140	27.30	2174	29.38	4113
145	27.80	2312	30.33	4398
150	28.30	2452	31.29	4694
155	28.78	2595	32.22	4994
160	29.24	2740	33.16	5306
165	29.71	2887	34.04	5617
170	30.15	3037	34.95	5942
175	30.60	3189	35.83	6270
180	31.03	3343	36.69	6604
185	31.42	3499	37.55	6947
190	31.87	3657	38.39	7294
195	32.27	3818	39.23	7650
200	32.65	3980	40.04	8008
205	33.05	4144	40.85	8374

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TABLE 4 (Continued)

Temperature (°K)	Cp (cal/mole °K)	$H-H_0$ (cal/mole)	$S-S_0$ (cal/mole °K)	$T(S-S_0)$ (cal/mole)
210	33.46	4310	41.67	8751
215	33.78	4479	42.45	9127
220	34.22	4648	43.24	9513
225	34.60	4820	44.01	9902
230	34.96	4994	44.77	10296
235	35.34	5170	45.51	10695
240	35.70	5348	46.28	11107
245	36.07	5527	47.02	11520
250	36.43	5708	47.74	11935
255	36.78	5892	48.48	12362
260	37.14	6067	49.20	12792
265	37.50	6263	49.89	13221
270	37.86	6451	50.61	13665
273.16	38.08	6571	51.05	13942
275	38.22	6640	51.30	14108
280	38.56	6833	51.99	14557
285	38.90	7027	52.69	15017
290	39.24	7223	53.36	15474
295	39.61	7420	54.02	15936
298.16	39.86	7545	54.45	16235
300	40.00	7619	54.69	16407
305	40.42	7820	55.36	16885
310	40.87	8023	56.03	17369
315	41.33	8229	56.68	17854
320	41.80	8437	57.35	18352
325	42.27	8648	57.99	18847
330	42.77	8860	58.64	19351
335	43.27	9076	59.28	19859
337.212	43.49	9172	59.57	20088
(Liquid)				
337.212	45.59	13760	73.17	24674
340	45.68	13888	73.55	25007
345	45.84	14118	74.22	25606
350	46.02	14348	74.89	26212
355	46.20	14579	75.54	26817
360	46.33	14811	76.18	27425
365	46.48	15044	76.83	28043
370	46.62	15278	77.45	28657

The following empirical equations represent these results (Columbia 13):

Solid Uranium Hexafluoride:

(37) $H-H_o = 9865.0 - 20.082\ T + 0.080790\ T^2 - \frac{1047920}{T}$ (See Fig. 3.)

(precision: ±0.01 per cent from triple point to 265°K; ±1 per cent from 265°K to 225°K)

(38) $S-S_o = 126.59 - 20.082 \ln T + 0.16162\ T - \frac{523960}{T^2}$ (See Fig. 4.)

(precision: -0.01 per cent from triple point to 273.16°K)

Liquid Uranium Hexafluoride:

(39) $H-H_o = 5986.6 + 17.954\ T + 0.032514\ T^2 - \frac{666990}{T}$

(precision: ±0.01 per cent)

(40) $S-S_o = -50.33 \quad 17.954 \ln T - 0.065028\ T - \frac{333490}{T^2}$

(precision: ± 0.01 per cent)

The errors given are the maximum deviation of the experimental values from those calculated from the equations.

British workers have determined a set of values for the specific heat of solid uranium hexafluoride (British 16,17), but these values probably are less precise than those given in Table 5. They also presented some values for the specific heat of liquid uranium hexafluoride (British 17) which are somewhat higher than the American values (e.g., C_p = 50 cal/mole °C at 353°K) and which can be represented by the formula,

(41) $Cp = 47.3 + 0.347(t-70)$ cal/mole °C), where t is in °C.

Additional British data for liquid uranium hexafluoride quoted by I. Kirschenbaum (Columbia 17), are given in Table 5.

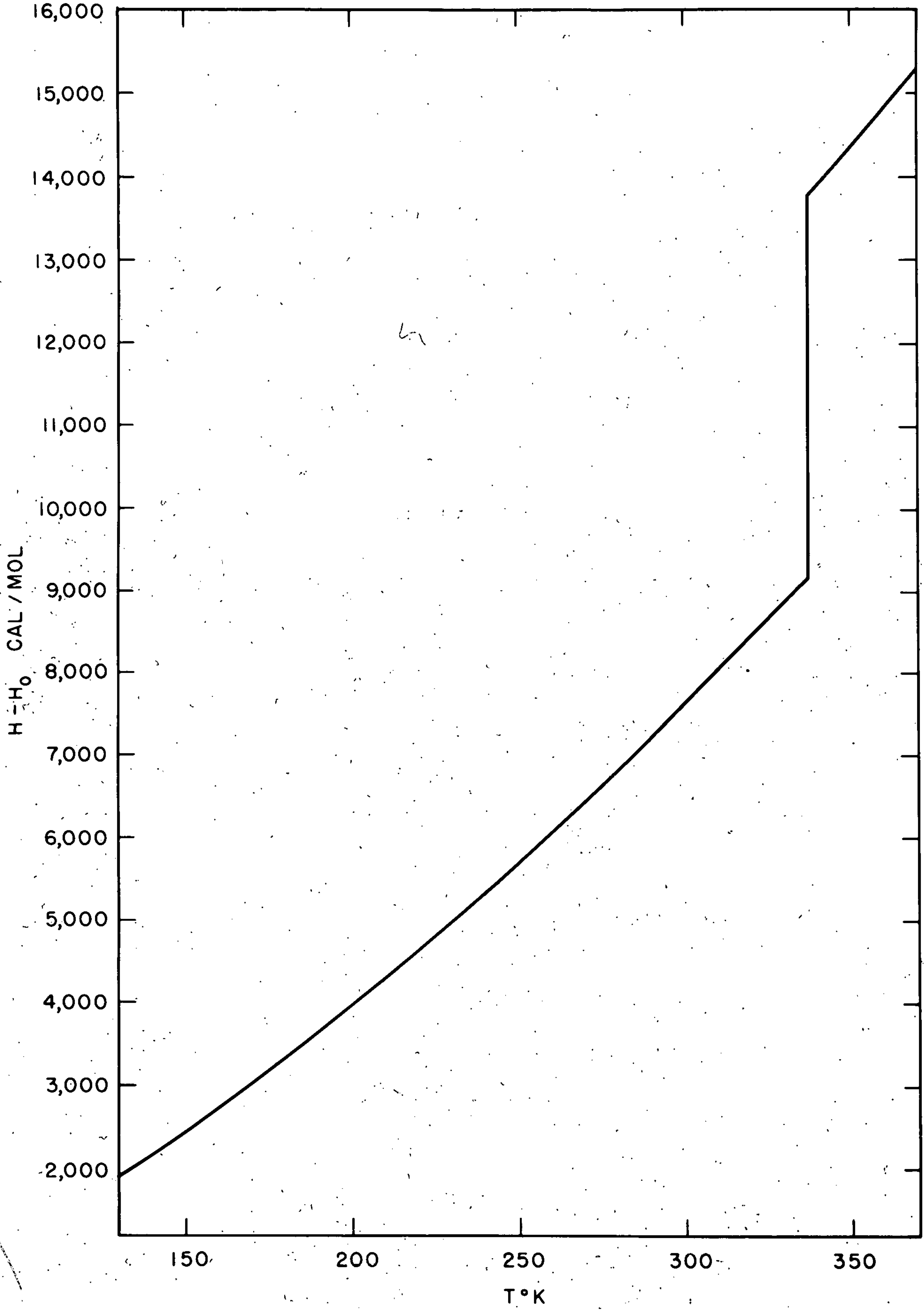

FIG. 3. ENTHALPY OF $UF_{6(S)}$ (SEE EQUATION 37.)

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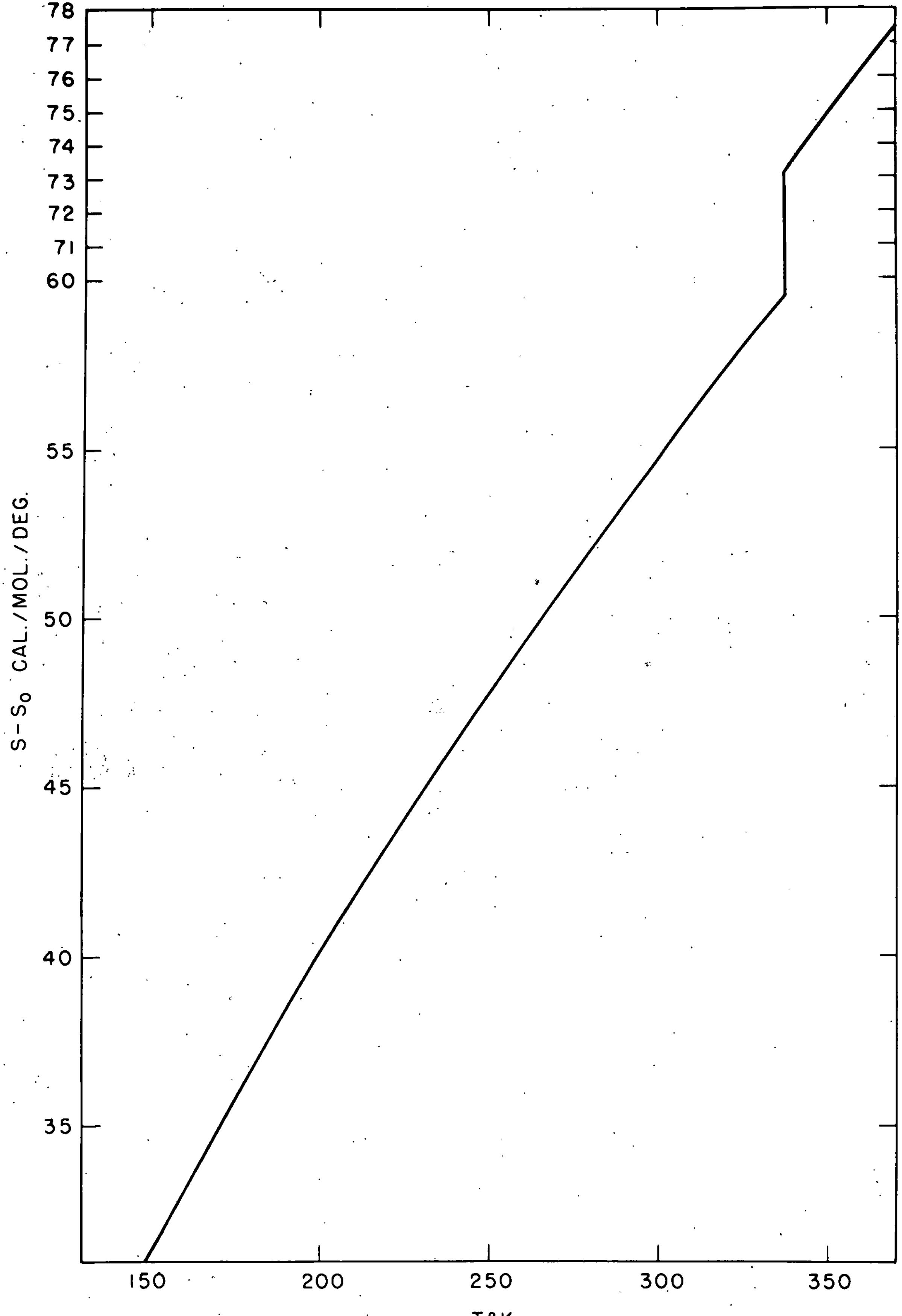

FIG. 4. ENTROPY OF $UF_{6(S)}$. (SEE EQUATION 38.)

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TABLE 5

SPECIFIC HEAT OF LIQUID URANIUM HEXAFLUORIDE

Temperature		C_p (cal/mole °C)
°C	°K	
65	338	47.0 ±1
70	343	47.4
80	353	48.1
90	363	48.8
100	373	49.5

At Columbia (18) the first values of the specific heat of uranium hexafluoride gas were obtained partly by direct measurement and partly by calculation from vibrational frequencies (the latter being determined by extrapolation from the measured infrared frequencies of SF_6, SeF_6 and TeF_6 using the U-X distance as parameter). Table 6 shows that the values obtained in this investigation were probably too low. More reliable are the specific heats obtained at Columbia (13) by calculation from the thermodynamical functions, equations (37), (38), (39), and (40), and the vapor pressure equations (29) and (33). The specific heat equation obtained in this way is:

(42) C_p (for $UF_{6(g)}$) = $32.43 + 0.007936\ T - \frac{320680}{T^2}$ cal/mole °C). (See Fig 5.)

The C_p values derived from this equation can further be compared with those calculated from the now experimentally determined vibrational frequencies of uranium hexafluroide and also with the more recent British calorimetric determinations (British 7, 16, 17). Table 6 shows that the values derived from equation (42) agree very well with the newer spectroscopic

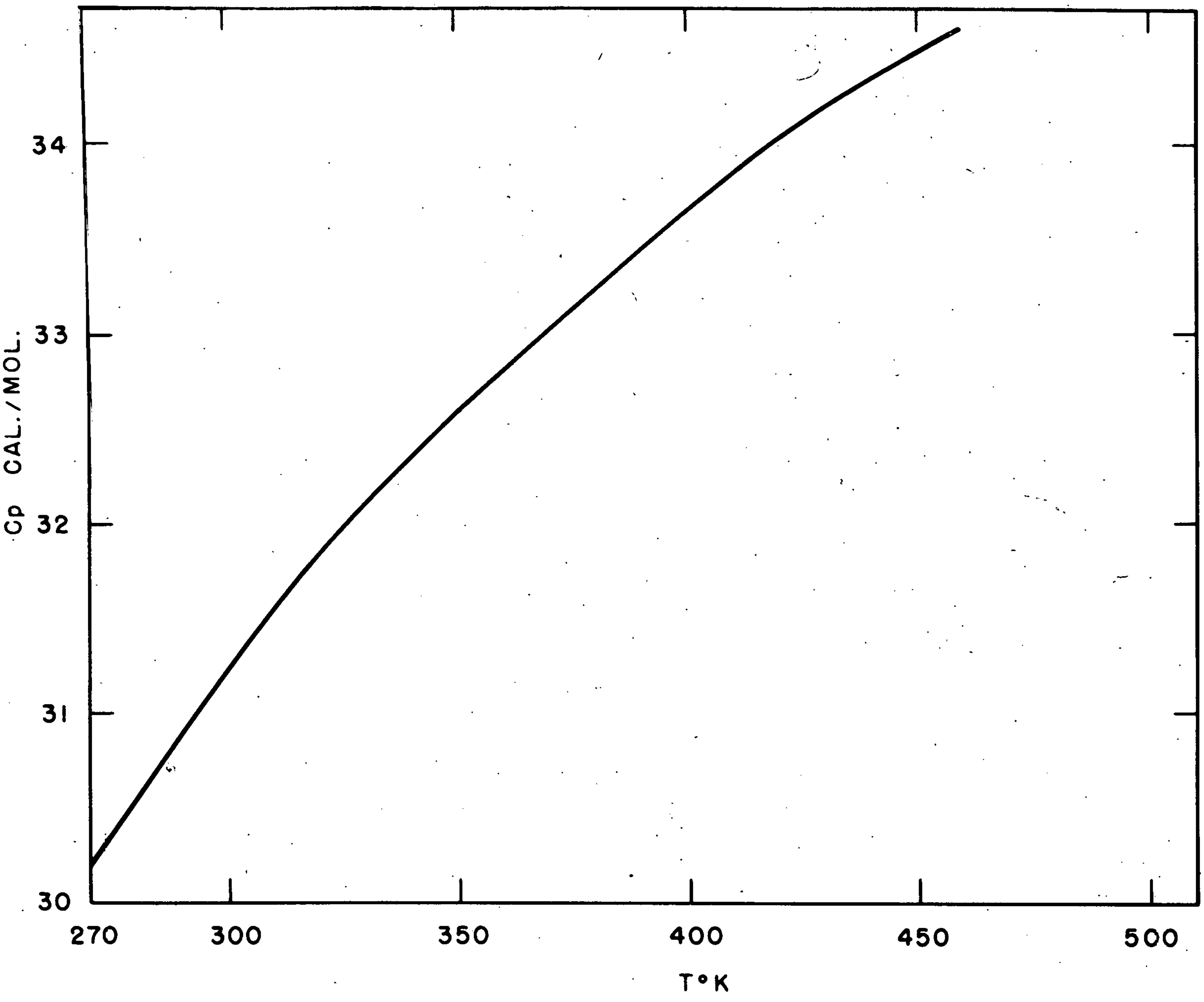

FIG. 5. HEAT CAPACITY OF $UF_{6(g)}$ AT CONSTANT PRESSURE.
(SEE EQUATION 42.)

results, but that the recent calorimetric values are considerably higher.

TABLE 6

SPECIFIC HEAT OF GASEOUS URANIUM HEXAFLUORIDE

Temperature (°C)	Cp (cal/mole °C)			
	(a)	(b)	(c)	(d)
25	33.5 -1.0	--	30.87	31.19
50	--	29.2 ±1.0	--	--
75	34.5 -1.0	30.1 ±1.0	32.23	32.54
100	--	30.8 ±0.5	--	--
125	35.5 -1.0	--	33.31	33.57

(a) Calorimetric determination.
(b) Spectroscopic frequencies extrapolated from SF_6.
(c) Spectroscopic measured frequencies.
(d) Calculated from thermodynamic functions (equation 42).

The heat content and the entropy of uranium hexafluoride gas have also been derived both by combination of the thermodynamical functions of the condensate with the vapor pressure equations (Columbia 13), and by theoretical considerations from the spectroscopic frequencies. The first method leads to the equations:

(43) $H = 8460 \quad 32.43\,T + 0.003958\,T^2 + \frac{320680}{T^2}$ cal/mole (See Fig. 6)

(44) $S\ (1\ \text{atm}) = 74.69 \log T + 0.007935 + \frac{1600340}{T^2} - 98.05$ e.u. (See Fig. 7)

The entropy values derived from equation (44) agree well with those calculated from infra-red data (Columbia 19) as shown by Table 7.

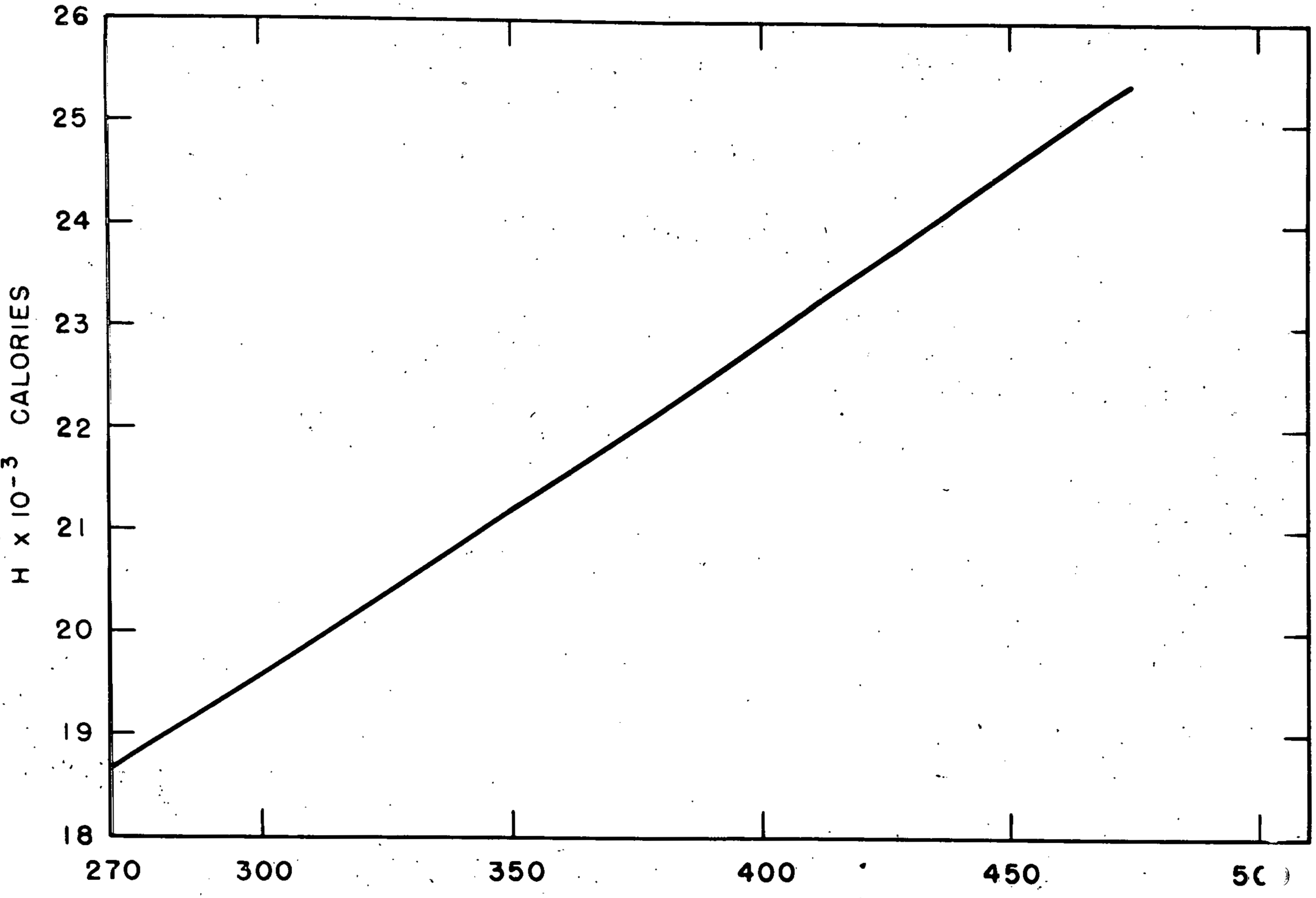

FIG. 6. ENTHALPY OF $UF_{6(g)}$. (SEE EQUATION 43.)

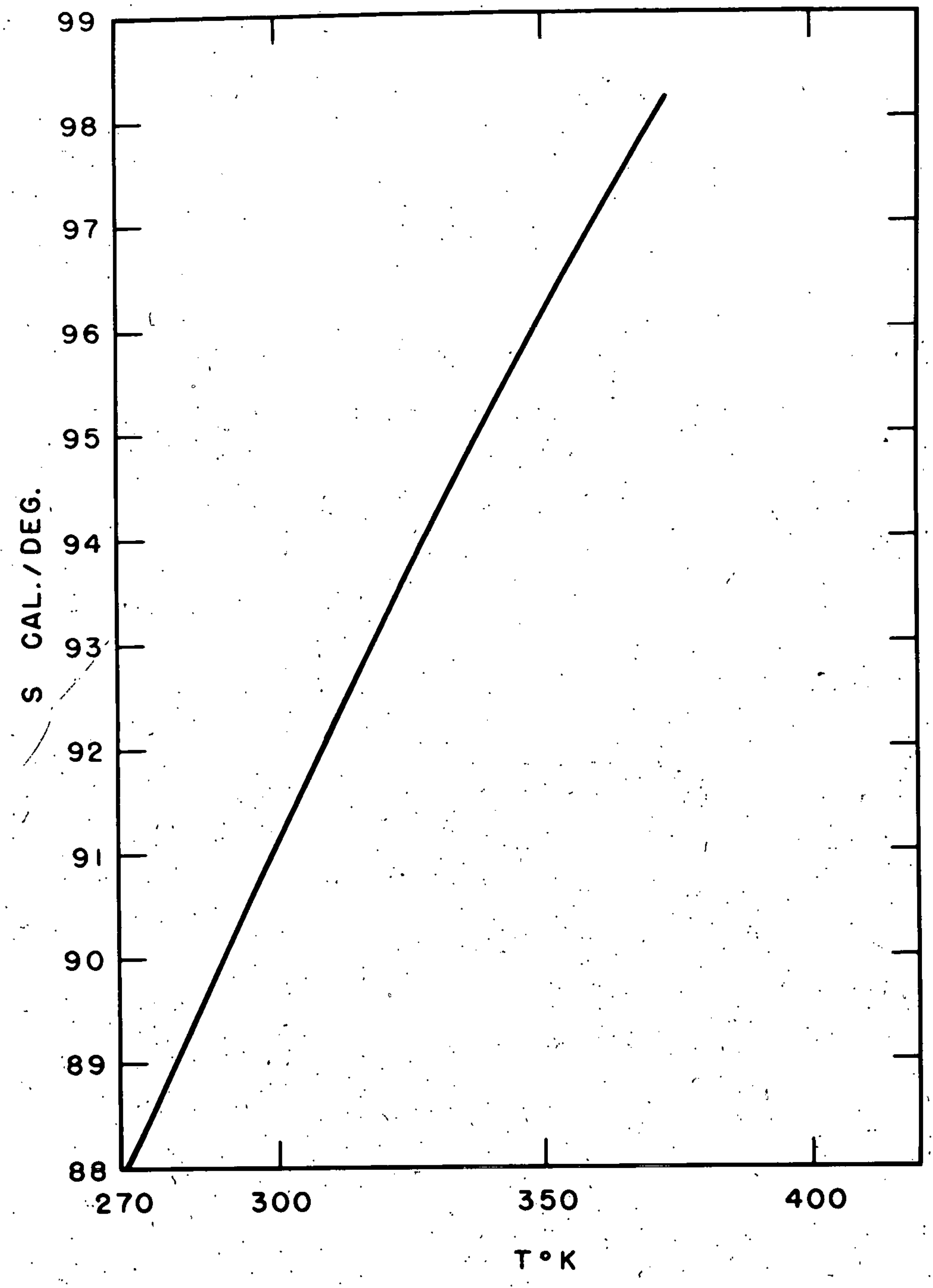

FIG. 7. ENTROPY OF $UF_{6(g)}$ AT ONE ATMOSPHERE. (SEE EQUATION 44)

TABLE 7

ENTROPY OF URANIUM HEXAFLUORIDE GAS

Temperature (°K)	ΔS (cal/mole °C) (a)	(b)	Temperature (°K)	ΔS (cal/mole °C) (a)	(b)
100	62.99	--	348	95.22	--
150	71.58	--	373	97.47	98.46
200	78.81	--	400	99.86	100.46
273	87.65	82.27	500	107.45	--
298	90.34	--	750	122.37	--
323	92.89	93.59	1000	132.58	--

(a) Values determined from spectroscopic frequencies.
(b) Values determined from Equation 44.

(c) Velocity of Sound in Gaseous Uranium Hexafluoride and the Ratio C_p/C_v. The velocity of sound in gaseous uranium hexafluoride has been measured by two British observers. One reported a mean value of 8,870 cm/sec at 49°C and pressures of 320 and 539 mm Hg (British 18), while the other found the velocity to be 8.990 cm/sec at 49.2°C and 420 mm Hg pressure (British 8).

Assuming deviations from the gas laws to be negligible, and using the value, $v = 8{,}990$ cm/sec, it is found that $(C_p/C_v) = 1.063 \pm 0.005$ (at 49.2°C). This agrees well with the value (1.066) which is obtained from equation (42) assuming the perfect gas laws to hold.

(d) Heat of Sublimation of Solid Uranium Hexafluroide. A value of 10.36 cal/mole for the heat of sublimation of uranium hexafluroide was reported by Ruff and Heinzelmann (1911). Two emperical formulae for this quantity have been derived from vapor pressure data:

(45) $\Delta H_{sublimation} = 20{,}400 - 0.00521\,T^3 + 0.3905\,T^2 - 98.66\,T$ cal/mole (British 17).

(46) $\Delta H_{sublimation} = -1405 + 52.512\,T - 0.076822\,T^2 + \frac{130800}{T}$ cal/mole (See Fig. 8) (Columbia 13).

Equation (46) derived from the vapor pressure formula (29) is probably the better of the two. Some additional data of British origin are given in Kirschenbaum's report, and are reproduced in Table 8 (Columbia 18).

TABLE 8

HEAT OF SUBLIMATION OF URANIUM HEXAFLUORIDE

(after British Measurements)

Temperature (°C)	$\Delta H_{sublimation}$ (kcal/mole)
-75	12.20 ± 0.10
-50	12.15 ± 0.10
-25	12.08 ± 0.10
0	11.98 ± 0.10
20	11.87 ± 0.10
40	11.73 ± 0.10
60	11.53 ± 0.10
65	11.47 ± 0.10

(e) Heat of Vaporization of Liquid Uranium Hexafluroide.

British investigators reported the following values for $\Delta H_{vaporization}$ as a function of temperature (British 9):

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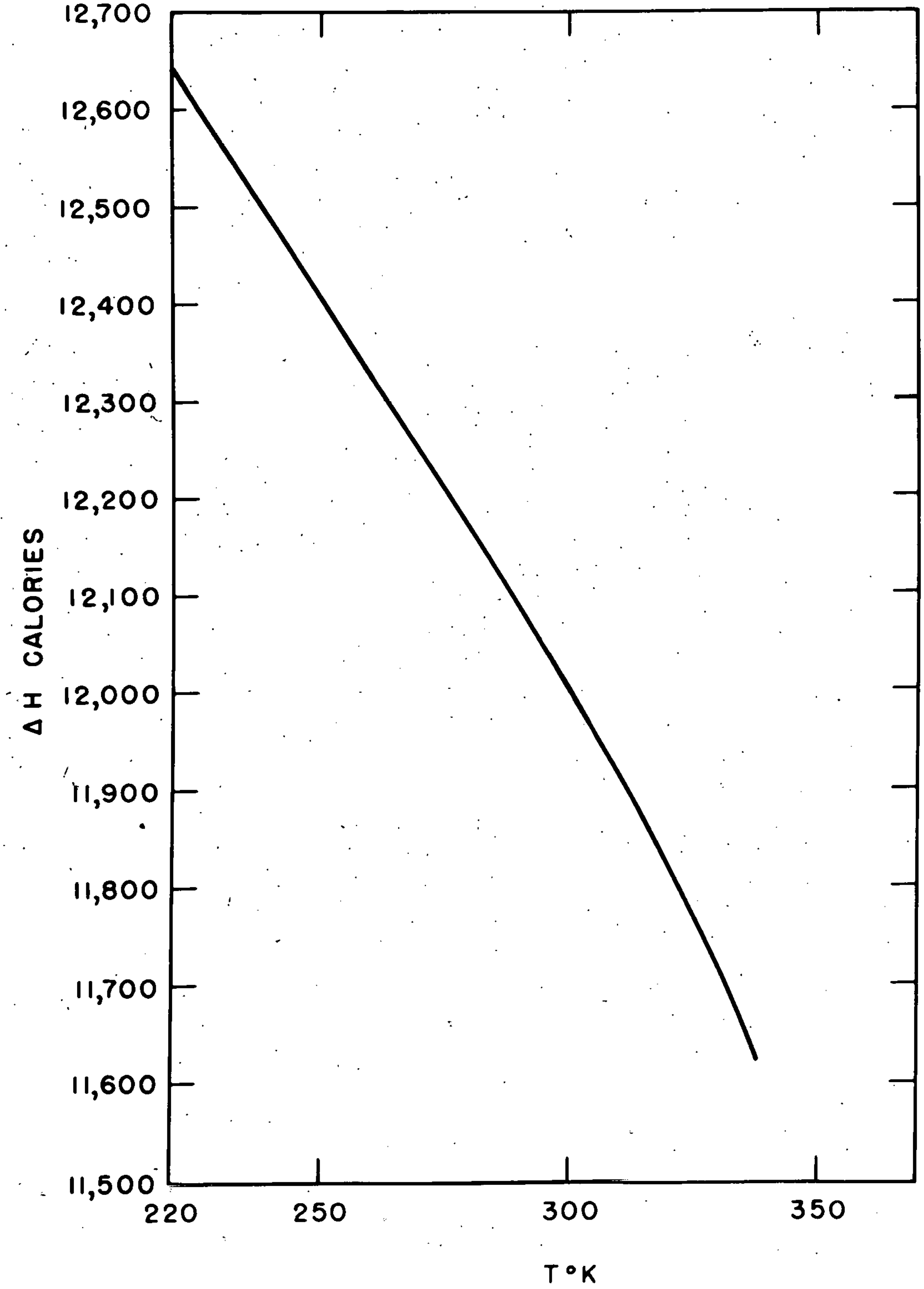

FIG. 8. HEAT OF SUBLIMATION OF $UF_{6(S)}$. (SEE EQUATION 46)

TABLE 9

HEAT OF VAPORIZATION OF URANIUM HEXAFLUORIDE

Temperature		ΔH vaporization (kcal/mole)	
(°C)	(°K)	(a)	(b)
65	338	6.95	6.92 ± 0.1
70	343	6.89	6.85 ± 0.1
75	348	6.82	--
80	353	6.74	--
85	358	6.66	--
90	363	6.57	6.67 ± 0.1
95	368	6.46	6.31 ± 0.1
110	383	--	--
130	403	--	5.80 ± 0.1

(a) (British 9).
(b) British results quoted by I. Kirschenbaum (Columbia 13).

The following equation for the heat of vaporization of liquid uranium hexafluoride was derived by Kirschenbaum (Columbia 13) from the vapor pressure equation (33):

$$\text{(47)} \quad \Delta H_{vap}\ (\text{cal/mole}) = 2473.4 + 14.476\,T - 0.02854\,T^2 + \frac{987670}{T}$$

(See Fig. 9)

(f) Heat of Fusion of Uranium Hexafluoride. The heat of fusion can be determined by direct calorimetric measurements, or calculated as the difference between the heat of sublimation of the solid and the heat of evaporation of the liquid. Table 10 gives a summary of the results obtained in these two ways.

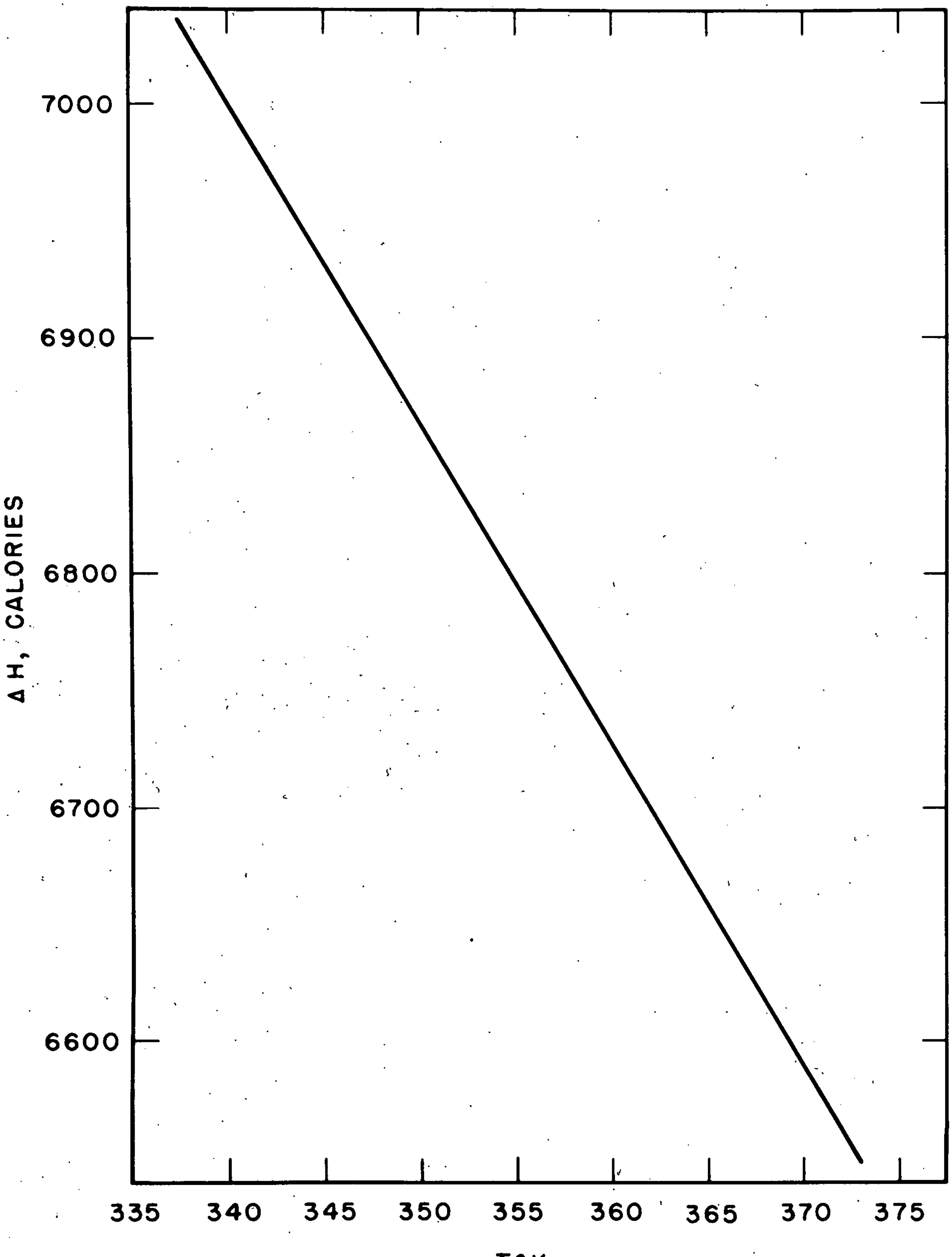

FIG. 9. HEAT OF VAPORIZATION OF $UF_{6(l)}$.
(SEE EQUATION 47.)

TABLE 10

HEAT OF FUSION OF URANIUM HEXAFLUORIDE

ΔH_{fusion} (kcal/mole)		Reference
Calorimetric Determination	$\Delta H_f = \Delta H_{subl.} - \Delta H_{vap.}$	
-	5.11 (= 12.00 - 6.89)	(Columbia 14)
-	4.60 (= 11.63 - 7.03)	(Columbia 13)
-	4.55 (= 11.47 - 6.92)	(British 17)
4.58	-	(British 9,16,19)
4.588	-	(Nat. Bur. Standards[2])

(g) Thermal Conductivity of Gaseous and Liquid Uranium Hexafluoride. A direct measurement of the thermal conductivity by the "hot wire" method has been made at the Carbide and Carbon Laboratory (SAM-Carbon and Carbide 3). The values were measured relative to argon and nitrogen, but in corresponding work carried out by the British, the reference gas is not named. This may account for the discrepancy between the British and American work. In Table 11 is given the thermal conductivity of $UF_{6(g)}$ at a number of temperatures. Included for comparison are values calculated from viscosity measurement by the Eucken equation:

$$(48) \quad K = \frac{1}{4}(9\gamma - 5)\frac{n\ C}{M}V$$

where γ = ratio of the specific heats at constant volume and pressure, n = viscosity, and the other symbols have their usual meaning.

TABLE 11

THERMAL CONDUCTIVITY OF URANIUM HEXAFLUORIDE GAS

(10^5 cal/cm sec °C)

Temperature (°C)	American[a]	British		From Viscosity Data[d]
		Old[b]	New[c]	
0	1.450	1.54	1.34	1.454
50	1.787	1.84	1.65	1.79
100	2.125	2.13	1.91	2.12
125	2.294	2.26	2.04	2.28

(a) SAM - Carbon and Carbide 3.
(b) British 20,21.
(c) British data (Columbia 17).
(d) SAM - Carbon and Carbide 4.

It can be seen that the American values obtained directly, column (a), and by calculation from viscosity data, column (d), are in excellent agreement. The four sets of data may be summarized analytically:

(49) American: $K = 1.542 + 0.0059t$ (10^5 cal/cm sec °C)

(50) British (old): $K = 1.454 + 0.0067t$ (10^5 cal/cm sec °C)

(51) British (new): $K = 1.39 + 0.0052t$ "

(52) From Viscosity: $K = 1.450 + 0.0067_5t$ "

These may be averaged to give equation (53), which probably represents the best available data for the thermal conductivity of the gas:

(53) $\overline{K} = 1.459 + 0.00614t$ (10^5 cal/cm sec °C)

One value for the thermal conductivity of $UF_{6(l)}$ has been given by Columbia workers (Columbia 20). This is a preliminary value of 3.83 ± 3% x 10^{-4} cal/(°C cm sec) at 72°C. No values for solid UF_6 are available.

2.3 Mechanical Properties

(a) Density of Solid UF_6. The density of $UF_6(s)$ was reported by Ruff and Heinzelmann to be 4.68 g/cc at 20.7°C (Ruff, 1911). From x-ray diffraction data, the Cornell group calculated first a density of 4.95 g/cc and later a more accurate value of 5.060 ± 0.005 g/cc (Cornell 1). British investigators found a density of 5.09 ± 0.06 g/cm at 20.7°C (British 10).

(b) Density of Liquid UF_6. The earliest measurement was made at Columbia University where the density of $UF_{6(l)}$ was found to be 3.667 ± 0.05 g/cc at 65.1°C (Columbia 21). At the National Bureau of Standards (4) the ratio of the liquid volume at 65.1°C to the solid volume at 63.5°C was found to be 1.343 ± .002, and equation (54) was given for the ratio of volume at the temperature, t, to the volume at the triple point, t_f.

(54) $V/V_f = 1 + 1.727 \times 10^{-3} (t - t_f) + 3.59 \times 10^{-6} (t - t_f)^2$.

Table 12 shows the measured and the calculated values of this ratio between 62.45°C and 52.4°C.

TABLE 12

RELATIVE SPECIFIC VOLUME OF LIQUID URANIUM HEXAFLUORIDE

$t-t_f$	V/V_f	
	(observed)	(observed-calculated)
-1.60	0.997	0.000
-0.02	1.000	0.000
0.92	1.001	-0.001
7.26	1.013	0.000
9.59	1.076	-0.001; 0.000
9.59	1.017	0.000
11.93	1.022	0.001
18.95	1.033; 1.034	-0.001; 0.000
21.29	1.038	0.000
25.98	1.048	0.001
28.33	1.053; 1.051	0.001; 0.001

Table 13 contains a summary of measured and calculated absolute densities of liquid UF_6. Column I gives values calculated from the expansion data of Table 12 using 3.630 g/cc for the density at 64.057°C. Column II was calculated in the same way using 3.667 g/cc for the density at 65.1°C. Column III contains a set of direct determinations made at Nat. Bur. Standards (3), and the values interpolated from these measured points by means of the empirical expression.

$$(55) \quad \rho = 3.630 - 5.805 \times 10^{-3} (t-t_f) - 1.36 \times 10^{5} (t-t_f)^2$$

$$(t_f = 64.052^\circ C)$$

The values which were experimentally determined are underlined. Column IV contains values which were not available to us in publications but were gathered from various summary reports issued by British and American groups (Columbia 13).

TABLE 13

DENSITY OF LIQUID URANIUM HEXAFLUORIDE

Temperature (°C)	Density (g/cc)			
	I	II	III	IV
65	3.624	3.667	3.624	-
68.66	-	-	3.604	-
70	3.593	3.636	3.595	-
72.91	-	-	3.576	-
75	3.561	3.604	3.565	-
77	-	-	-	3.63 ± 0.18
80	3.530	3.572	3.532	-
85	3.498	3.540	3.502	-
90	3.464	3.508	3.470	-
92.65	-	-	3.452	-
95	-	-	3.437	-
100	-	-	3.404	-
112.67	-	-	3.316	-
120	-	-	3.263	-
131.12	-	-	3.183	-
140	-	-	3.111	-
156	-	-	-	3.11 ± 0.16
160	-	-	2.948	-
162.59	-	-	2.920	-
203	-	-	-	2.62 ± 0.13
215	-	-	-	2.32 ± 0.12
225	-	-	-	2.09 ± 0.10
230	-	-	-	1.63 ± 0.08

DECLASSIFIED

(c) Density of $UF_{6(g)}$. Gaseous UF_6 behaves like a nearly perfect gas. There is no evidence for any association. Ruff and Heinzelmann (1911) found an average molecular weight of 338 in two vapor density determinations at 448°C. More recent determinations have been made by British investigators (British 8). Without giving detailed data one of them stated that there is no systematic dependence of molecular weight on temperature or pressure, and that the weighted average corresponds to a molecular weight of 353.2 (the theoretical value is 352.1 with an average error of ±1.3. Thirteen experiments were made at 18°C, four at 68°C, and one each at 83°C and 96°C; (pressures ranged from 1.6 to 18 mm Hg and were determined with a Bourdon gauge used as a null instrument.) Other British workers also found values very close to the theoretical for non-associated UF_6 (British 22,23). They determined the gas density at 50°C as a function of pressure. (See Table 14.) When this data is plotted, an almost straight line results. The slope

$$\left(\frac{\partial \rho}{\partial p}\right)_{T = 49.2^{\circ}C} \qquad \begin{matrix}(\rho = g/cc)\\(p = dynes/cm^2)\end{matrix}$$

was found to be $1.32 \pm 0.1 \times 10^{-8}$ which agreed excellently with the theoretically computed value of 1.314×10^{-8} for a perfect gas with the UF_6 molecular weight.

TABLE 14

VAPOR DENSITY OF URANIUM HEXAFLUORIDE AS A FUNCTION OF THE PRESSURE AT 50°C

Vapor Density (10^3 g/cc)	Pressure (10^{-5} dynes/cm^2)
9.016	7.027
5.295	4.246
6.482	5.072
7.240	5.717
8.119	6.315
4.278	3.479
3.627	2.862
3.130	2.534

Since UF_6 behaves like a perfect gas, its density at various temperatures and pressures can be calculated from equation (56) (Columbia 15):

$$(56) \qquad \rho_{(g/cc)} = 13.28 \; \frac{323.2}{T°K} \times \frac{(\text{cm Hg})}{76.0}$$

(d) Self-Diffusion Coeffecient of $UF_{6(g)}$. The Virginia Group determined a value of 234 ± 9 micropoise at 30°C for the product $\rho \cdot D$, where ρ = density, and D = self diffusion coefficient (Virginia 1). Since according to equation (56) the density at 30°C is:

$$(57) \quad \rho = (13.28 \times \frac{323.2}{303.2} \times \frac{15.5}{76.0} = 2.887 \text{ g/l},$$

one finds:

$$(58) \quad D = \frac{0.000234}{0.002887} = 0.081 \text{ cm}^2/\text{sec}.$$

This makes it possible to calculate a value for ϵ from the equation, $\rho D = \epsilon \eta$, where η = viscosity coefficient. According to British data, $\eta_{30^\circ C}$ = 180 micropoises, while Columbia University data indicate $\eta_{30^\circ C}$ = 206 micropoises (See Sec. 2.3 f). The value of ϵ for UF_6 therefore is either 1.30 or 1.14. The large difference between these two values indicates the need for renewed study. The kinetic theory of gases shows that ϵ should be 1.200 for hard sphere molecules and 1.504 for molecules interacting as the inverse fifth power of distance. A theoretical formula for $D_{(UF_6)}$ has been derived using the value ϵ = 1.50 (Columbia 15):

$$(59) \quad D = (0.0606) \frac{20.0 \text{ cm}}{P_{\text{cm Hg}}} \left[1 + 6.29 (t \times 10^{-3}) + 9.6 (t \times 10^{-3})^2\right] \frac{\text{cm}^2}{\text{sec}}$$

but the uncertainty of this value restricts the usefulness of the equation.

(e) Mean Free Path. The following formula has been given for the mean path, L of UF_6 molecules in the gas phase:

$$(60) \quad L = \frac{20.0 \text{ cm}}{P_{\text{cm Hg}}} \times 6.32 \left[1 + 4.45(t\times10^{-3}) + 3.1(t\times10^{-3})^2\right] \times10^{-6}\text{cm}$$

(t = °C from 0° to 200°C)

Values for the mean free path calculated from the equation

$$L = \frac{1}{\sqrt{2}\,\pi N \sigma^2}$$

where σ, the molecular diameter, is derived from viscosity measurement, check fairly well with those computed from equation (60).

(f) Viscosity of UF_6. The Columbia group measured the viscosity of liquid UF_6 from 67.2°C to 75.0°C and found the values given in Table 15 (Columbia 22). The absolute viscosity of UF_6 is a little less than twice as large as that of water (0.422 centipoise at 67.2°C); the kinematic viscosity is about one-half as large (η_{H_2O} at 67.2°C is 0.431 centipoise).

TABLE 15

VISCOSITY OF LIQUID URANIUM HEXAFLUORIDE

Temperature (°C)	Absolute Viscosity (centipoises)	Kinematic Viscosity (centistokes)
67.2	0.731	0.200
70	(0.91)	--
72.5	0.692	0.191
72.9	0.685	0.189
73.4	0.679	0.188
74.7	0.669	0.185
75.0	0.663	0.184
80	(0.85)	--
90	(0.80)	--
100	(0.75)	--

The results of British measurements, given in parentheses in Table 15 (Columbia 17), do not agree well with those obtained at Columbia.

The viscosity of gaseous UF_6 has been measured by British workers (British 20,21,24). For the temperature range 0°-200°C, the following relationship was found to reproduce the data in Table 16 (column 1) to within ± 2 percent.

(61) $\eta\ 10^4$ poise $= 1.67 - 0.0044T$ $(t = {}^\circ C)$

At Columbia University, however, a determination of the viscosity of gaseous UF_6 gave results which differed by 20 per cent from those of the British (Columbia 23). A recent redetermination at the Carbide and Carbon Laboratory (SAM- Carbon and Carbide 5) has shown that the British values are substantially correct. Sutherland's constant has been computed from the British data and is found to be about 101 (British 10).

TABLE 16

VISCOSITY OF GASEOUS URANIUM HEXAFLUORIDE

Temperature (°C)	Viscosity (micropoises)	
	British	SAM-Carbide and Carbon
0	167	--
20	175	--
40	--	178.7
50	189	--
60	--	189.0
80	--	199.9
100	211	--
110	--	216.1
140	--	231.9
150	233	--
170	--	248.0
200	255	261.1

(g) Surface Tension of Liquid UF_6. The surface tension of liquid UF_6 in equilibrium with its vapor has been measured by British workers using the capillary rise method in the temperature range 70.0°C to 100°C (British 14). The results are summarized in Table 17.

TABLE 17

SURFACE TENSION OF LIQUID URANIUM HEXAFLUORIDE

Temperature (°C)	Surface Tension (dynes/cm)
70	16.8 ± 0.3
80	15.6 ± 0.3
90	14.3 ± 0.3
100	13.1 ± 0.3

2.4 Optical Properties

(a) Refractive Index (British 25). The refractive index of liquid UF_6 has been determined from 70°C to 100°C by measurements of the angle of total reflection and is probably accurate to 0.4 per cent in absolute value. The relative values are probably better than this. The results are summarized in Table 18.

TABLE 18

REFRACTIVE INDEX OF LIQUID URANIUM HEXAFLUORIDE

Temperature (°C)	Refractive Index	
	4360 A°	5890 A°
70	1.383	1.367
80	1.374	1.358
90	1.365	1.350
100	1.355	1.342

The molecular refraction, R, was calculated from the well-known expression:

(62) $$R = \frac{M}{\rho} \frac{(n^2 - 1)}{(n^2 + 2)}$$

(M = molecular weight)
(ρ = density)
(n = wave length of light).

The results are $R_{4360\ A^\circ} = 22.59 \pm 0.08$ ($t = 85^\circ C$)

$R_{5890\ A^\circ} = 21.83 \pm 0.08$ ($t = 85^\circ C$)

On the assumption that the molecular refraction of the vapor is the same as that of the liquid, the index of refraction of the gas at 5100 A° should be (British 10):

(63) $$n - 1 = 5.2 \times 10^{-4}\ P_{mm}/T^\circ K$$

(b) Ultra-Violet Absorption Spectrum of UF_6. The ultra-violet absorption spectrum of UF_6 vapor was first photographed by Lipkin and Weisman (MP Berkeley 1) with a large Hilger instrument (dispersion 5 A° per mm). A one meter layer of the vapor in equilibrium with the solid at room temperature was used. Strong continuous absorption was found to set in at about 3300 A°; it was preceded by a region of banded absorption between 3400 A° and 3800 A°. No analysis of the spectrum was made.

Martin and Amphlett (British 26) also examined the ultraviolet absorption of UF_6 vapor at room temperature, and found strong selective absorption, with a band head at 3701 A° and a minimum at about 3417 A°.

The absorption spectrum in the region 3500 - 4000 A° was then again studied at Columbia (24). The UF_6 gas was at a pressure of 36 mm, and a path length of 102 cm was used. The five most prominent bands appear to be separated by about

590 cm^{-1} (Table 19). Around each of the main bands there are groups of closely spaced bands, separated by frequencies of the order of 100 cm^{-1}. In addition there are apparently four bands separated from the main bands by about 200 cm^{-1}. It was further reported that a thick layer (12 cm) of clear crystalline solid UF_6 showed complete absorption below 4271 A° (Columbia 25). The UF_6 absorption at 42000 cm^{-1} is about 1000 times stronger than that in the band region discussed here. It is continuous and extends, with gradually declining intensity, to about 31000 cm^{-1}. A magnetic field of 19,000 gauss was found to have no effect on the spectrum.

TABLE 19

ABSORPTION BANDS OF URANIUM HEXAFLUORIDE GAS

Frequency (cm^{-1})			
24364	25478	26755	27655
24460	25538	26935(d)	27820(b)
24504	25720	27015(c)	27907
24794	26031	27135	28080
24860	26175	27184	28415(e)
24972	26227	27234(a)	
25108	26379	27342	
25211(f)	26573	27420	
25344	26644	27562	

(a) strongest absorption (violet edge) (d) doubtful
(b) strong absorption " " (e) center
(c) moderately strong " " (f) somewhat sharper

(c) Fluorescence Spectrum Of UF_6 (Columbia 26). Solid UF_6, excited by λ 3660 A°, shows a bright violet fluorescence at 77°K which disappears at room temperature. No fluorescence could be observed in UF_6 vapor even with long exposures. The fluorescence spectrum shows diffuse bands with a separation of about 220 cm^{-1}. The maximum of intensity appears to be near 23,700 cm^{-1}; the range covered is 22,000 to 24,700 cm^{-1}. A magnetic field of 25,000 gauss had no effect on the fluorescence spectrum.

TABLE 20

FLUORESCENCE BANDS OF SOLID URANIUM HEXAFLUORIDE AT 77°K

Frequency (cm^{-1})	
22230	23319
22450	23537
22662	23739
22883	23994
23098	24166

(d) Infra-Red Absorption and Raman Spectra. The infra-red spectrum of $UF_{6(g)}$ has been studied by J. Turkevich (Columbia 13) with results which are summarized in Table 21.

TABLE 21

INFRA-RED ABSORPTION BANDS OF GASEOUS URANIUM HEXAFLUORIDE

Frequency (cm^{-1})	μ	Intensity
632	16.05	100
675	14.82	10
713-719	14.03-13.91	1/2
825	12.12	2
850	11.68	1/4
1163	8.60	4
1295	7.72	3
2053	4.87	1/2

The Raman spectrum has also been studied. The Columbia Group reports that liquid UF_6 at 70.9°C gives two Raman lines at 603 cm^{-1} and 228 cm^{-1} on 3 hour exposure to the mercury line 4358.34 A° (Columbia 27). The most intense line is at 603 cm^{-1}. Another line at 572 cm^{-1} was predicted but was not found; it is, perhaps, masked by the line at 603 cm^{-1}.

Another detailed study of the Raman spectrum has also been made at Columbia (19).* A number of experiments were performed using 4358 A° excitation. Despite efforts to reduce photodecomposition of the liquid UF_6, a sufficient amount of fine fluffy solid formed in 15 minutes to necessitate stopping the exposure, because

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* The apparatus used was that of the American Cyanamide Co. at Stanford, Conn.

of the scattering of light by the solid. It was impossible to determine whether or not there were any Raman lines below 300 cm^{-1}. Two Raman lines were found outside this region. The average values obtained from exposures of the liquid were 656 ± 3 cm^{-1} and 511 ± 3 cm^{-1}. The high frequency line was sharp and strong, while the lower frequency line was quite weak and somewhat diffuse. Attempts were made to extend the data by the use of UF_6 solutions in fluorocarbons. With 4358 A° radiation photodecomposition still took place as with pure hexafluoride. With 5460 A° radiation, no decomposition was evident, and a satisfactory Raman spectrum was obtained. A strong line at 202 cm^{-1} was found in addition to the line previously found at 656 cm^{-1}. The line at 511 cm^{-1} did not appear, probably because of low intensity, and the 656 cm^{-1} line was shifted to 666 cm^{-1} in the fluorocarbon solution.

The infra-red and Raman data have been analyzed by Mayer and Bigeleisen (Columbia 19). The infra-red data indicate that there may be an accidental degeneracy. It is assumed that the fundamental frequency is about 640 cm^{-1}, that a double overtone falls at about the same point, so that the two lines at 623 cm^{-1} and 675 cm^{-1}, originate from the interaction of two levels at about 640 cm^{-1}. The following frequency assignment was made on this assumption.

TABLE 22

FREQUENCY ASSIGNMENT FOR GASEOUS URANIUM HEXAFLUORIDE BASED ON RAMAN SPECTRA

Frequency		Symmetry	Degeneracy	Activity	Observed
ν_1	656	A_{1g}	1	Raman Active	656 ± 3
ν_2	511	E_g	2	"	511 ± 3
ν_3	200	T_{2g}	3	"	202 ± 3
ν_4	130	T_{2u}	3	Inactive	———
ν_5	200	T_{1u}	3	Infra red active	———
ν_6	640	T_{1u}	3	Infra red active	623 or larger

Calculated and observed infra-red active double overtones are compared in Table 23.

TABLE 23

CALCULATED AND OBSERVED INFRA-RED OVERTONES

Calculated		Observed	Strength
ν_5	200 cm^{-1}	--	
$\nu_4 + \nu_5$	300	--	
$\nu_5 + \nu_3$	400	--	
ν_6	640	?632? 623	1000
$\nu_4 + \nu_2$	641	675	10
$\nu_5 + \nu_2$	711	713-719	1/2
$\nu_6 + \nu_3$	840	825	2
$\nu_5 + \nu_1$	856	850	1/4
$\nu_6 + \nu_2$	1151	1163	4
$\nu_6 + \nu_1$	1296	1295	3
		2053	1/2

2.5 Electrical and Magnetic Properties.

(a) Dielectric Constant. Martin and Amphlett reported the dielectric constant of $UF_{6(g)}$ at room temperature and atmospheric pressure to be 1.004 (British (26). They later revised this value to 1.0043 ± 0.001 (British 10). A careful determination at Princeton University gave the following results (Princeton 1) :

TABLE 24

DIELECTRIC CONSTANT OF GASEOUS URANIUM HEXAFLUORIDE

Temperature (°C)	Dielectric Constant ϵ	Molecular Polarization P
59.5	1.00297 ±.00006	27.0 ± 0.2
67.4	1.00292 ±.000003	27.2 ± 0.3
89.0	1.00273 ±.00005	27.0 ± 0.2

From a knowledge of the dielectric constant, ϵ, of the gas, the molar polarization can be calculated, and from this, in turn, by the use by the Clausius-Mosotti equation,

(54) $$P = \frac{M}{\rho} \cdot \frac{\epsilon - 1}{\epsilon + 2},$$

one can obtain the dielectric constant of the liquid. The British calculated values of $P = 34$ and $\epsilon = 2.6$ for the liquid (British 10). The Princeton group reported $P = 27.1$ and $\epsilon = 2.18$ at 65°C. These values are typical of nonpolar liquids.

(b) Dipole Moment. Smyth and Hannay (Princeton 1) have calculated the dipole moment of gaseous UF_6 at various temperatures from the dielectric constant. It was found (See Table 24) that the molar polarization, P, does not vary with temperature. P is defined by the well-known Debye relationship:

$$(65)\quad P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3}\alpha + \frac{4\pi N\mu^2}{9kT}$$

The absence of any significant variation of P with temperature indicates that the dipole moment is probably zero. By the usual criteria it is concluded that, while UF_6 could have dipole moment of $< 0.5 \times 10^{-18}$, it is logical to assume that its moment is zero.

(c) Magnetic Susceptibility. Uranium hexafluoride appears to be paramagnetic. Henkel and Klemm (1935) found the specific susceptibility of solid UF_6 to be $+0.12 \times 10^{-6}$ and the molar susceptibility $+43 \times 10^{-6}$. With the molar susceptibility corrected for diamagnetism (U = 23, F = 7.25) (Tilk, 1939), a value of $+106 \times 10^{-6}$ is obtained. The paramagnetism seems to be independent of the temperature.

(d) Ionization Potential. The critical ionization potentials of the monovalent ions produced by slow electron bombardment of UF_6 have been determined (CEW-TEC 4):

TABLE 25

CRITICAL IONIZATION POTENTIALS OF UF_6 GAS

Ion	Potential (volts)	Ion	Potential (volts)
UF_5^+	15.5	UF_2^+	29.9
UF_4^+	20.1	UF_1^+	37.9
UF_3^+	23.5	UF^+	50.3

2.6 Structure of Uranium Hexafluoride Molecule. The structure of uranium hexafluoride has been studied by electron diffraction, x-ray crystallography, Raman spectrum, infra-red spectrum, and dipole moment. The evidence available indicates that UF_6 possesses an undistorted octahedral structure.

(a) Electron Diffraction Studies. Electron diffraction studies of UF_6 were first carried out by Braune and Pinnow (1937). They reported irregular structures for the hexafluorides of uranium, tungsten, and molybdenum, possessing holohedral orthorhombic symmetry, the three pairs of M-F distances having the ratios 1:1.12: 1.22. For the uranium compound, this leads to 1.78, 1.99 and 2.17 A° for the metal-fluorine distances. Bauer (Columbia 28) investigated the electron diffraction of UF_6 vapor, using 42 kv electrons, and concluded that all six U-F distances could not be identical. Two models could be reconciled with his data. (The symmetrical octahedral structure as well as several other possible structures were excluded.) Bauer selected as the most probable structure a deformed octahedron with the fluorine atoms at six corners, and the uranium atom in the plane of 4 fluorine atoms. The interatomic distance for this model are:

Two adjacent U - F = 1.87 ± 0.02 A°
Two opposed U - F = 2.12 ± 0.03 A°
Two adjacent U - F = 2.22 ± 0.03 A°

The distortion is in a direction as to produce nearly equal F-F separations (about 2.9 A°). This structure is similar to that of Braune and Pinnow, but the absolute values of the interatomic distances are larger by approximately 5 per cent.

The model proposed by Bauer has no center of symmetry and must therfore have a small dipole moment. The analgoy to the structure of uranium metal found by Jacob and Warren (1937) is clear.

(b) Dipole Moment. Smyth (Princeton 1) pointed out that the structure proposed by Bauer necessitated a dipole moment of not less than 1.5×10^{-18} and probably larger. Measurement of the dielectric constant showed the moment to be no larger than 0.5×10^{-18}, and very likely, zero. This renders Bauer's proposed structure untenable. Smyth further pointed out that one of the models Bauer had discarded fitted the electron diffraction data quite well. This structure has undistorted octahedral angles with interatomic distances:

Two opposed U - F = 1.87 A°

Two opposed U - F = 2.12 A°

Two opposed U - F = 2.22 A°

This structure would have three pairs of mutually opposing and canceling dipoles, which would give zero moment to the molecule as a whole.

(c) Evidence from Raman and Infra-red Spectra (Columbia 19,25,26,27). The appearance of only three Raman lines is strong evidence for a symmetrical octahedral structure for UF_6, since for any other model, more lines should appear. If the UF_6 molecule is a regular octahedron, it belongs to symmetry group O_h and selection rules show that only three Raman lines are to be expected; a tetragonal octahedron (D_{4h} or C_{4v}) would give a much larger number of lines. Only a plane hexagon (D_{6h}) would give an equally small number of lines as the regular octahedron. It has further been pointed out that even if only two opposite uranium-fluoride bonds were elongated, the Raman lines at 511 cm^{-1} and 202 cm^{-1} should be split. No such splitting is observed. The infra-red spectrum shows only one fundamental frequency between 600 and 2100 cm^{-1}, and this also can be explained on the basis of complete octahedral symmetry.

(d) X-Ray Crystal Structure (Cornell 1). X-ray analysis of cylindrical single crystals show that $UF_{6(s)}$ possesses orthorhombic holohedry, space group D_{2h}^{16} - Pnma. At 24°C, the parameters are: $a = 9.900 \pm 0.002$ A°, $b = 8.962 - 0.002$ A°, and $c = 5.207 \pm 0.002$ A°. The unit cell contains four molecules and the x-ray density of the solid UF_6 at 25°C is 5.060 ± 0.005 g/cc. A comparison between experimentally determined and "ideal" parameters for this structure is given in Table 26.

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TABLE 26

COMPARISON OF EXPERIMENTALLY DETERMINED AND "IDEAL" PARAMETERS OF THE URANIUM HEXAFLUORIDE STRUCTURE

Atom	Parameters					
	Experimental			Ideal		
	X	Y	Z	X	Y	Z
U	0.1295	1/4	0.081	1/8	1/4	1/2
F_I	0.003	1/4	-0.250	0	1/4	-1/4
F_{II}	0.250	1/4	0.417	1/4	1/4	5/12
F_{III}	0.014	0.093	0.250	0	1/12	1/4
F_{IV}	0.246	0.093	-0.083	1/4	1/12	-1/12

The x-ray data do not indicate a completely regular octachedral configuration for the molecule as it exists in the crystal. The fluorine atoms are in approximately closest packing; there appears to be a real but small deviation from ideal symmetry in a slight flattening of the molecule along the normal to the plane of symmetry. This slight distortion may be the result of non-isotropic vibrations in the crystal and is compatible with a perfectly regular configuration of the molecules in the vapor. The configurations favored by Bauer for the vapor are definitely excluded for the crystal.

3. Chemical Properties of Uranium Hexafluoride

Uranium hexafluoride is a highly reactive substance. Its chemical properties will be discussed under three headings: 3.1 General chemical behavior; 3.2 Soltions of uranium hexafluoride in various solvents; 3.3 Corrosive effects on metals and other materials of construction.

3.1 General Chemical Behavior.

(a) Water. UF_6 reacts vigorously with water, forming mainly UO_2F_2 and HF. Considerable heat is evolved in this reaction. (See Sec. 2.2a.) When working on a large scale, it is advantageous to carry out the hydrolysis by introducing UF_6 into dilute alkali, either as vapor, or by liquefying UF_6 vapor and allowing drops to fall into the "drowning vessel." Rough calculations indicate that the heat of solution of UF_6 in dilute sodium hydroxide is about -118 kcal/mole (duPont 2).

The reaction of UF_6 with NaOH proceeds as follows:

(66) $UF_6 \quad 4OH^- \longrightarrow UO_2^{++} + 6F^- + 2H_2O$ (pH 7.0-7.5)

(67) $2UO_2^{++} + 6OH^- + 2Na \longrightarrow Na_2U_2O_7 + 3H_2O$ (pH 10.0-10.5)

At a partial pressure of 15 mm of UF_6, the reaction with water vapor gives a dense white smoke which settles rapidly. At 0.4-0.5 mm UF_6 no smoke is visible (British 27). X-ray studies showed that interaction of UF_6 with H_2O vapor does not give pure UO_2F_2, but rather a complex of UO_2F_2, HF and H_2O, from which pure UO_2F_2 can be obtained by heating to 180°C or higher (British 28). This statement probably requires verification.

(b) Oxygen, Nitrogen and Carbon Dioxide (Ruff 1911). UF_6 is completely stable to oxygen, nitrogen, and dry air. No reaction occurs with CO_2, but caution must be exercised since fluorination to carbonyl fluoride and subsequent explosion may occur.

(c) Halogens (Ruff, 1911). UF_6 is soluble to a considerable extent in liquid chlorine and bromine; it does not react with gaseous chlorine or bromine either in the cold or upon heating. The behavior of iodine has not been studied.

(d) Reduction of Uranium Hexafluoride by Non-Metals (MP Ames 1). Ruff and Heizelmann stated that UF_6 reacts with hydrogen instantaneously at room temperature. However, more recently, repeated attempts to reduce UF_6 with hydrogen have all resulted in failure. Thus, the Ames Group found no reaction below 390°C. Even above 500°C reaction was only moderately fast and incomplete, leading to a complex mixture of products (MP Ames 2). Addtition of a small amount of chlorine did not catalyze the reduction. Similar observations have been made by British workers, who found that the reaction of UF_6 with H_2 required a considerable energy of activation; reaction could be initiated, for example, by ultra-violet light or by electrical discharge. Various materials were tried as catalysts. Among them were H_2O, UF_4, Br_2, I_2, UN_2, Ni, UCl_4, Cl_2, HCl, Hg_2Cl_2, and $FeCl_3$, but only the chlorides had any appreciable effect. Even in their presence, reaction is slow and only impure products have been isolated (British 25,28).

Sulfur dioxide failed to reduce UF_6 when passed through UF_6 either at room temperature, or on heating the gaseous mixture in a nickel tube to 150°C (MP Ames 3). Ethylene, under the same conditions, apparently reduced UF_6. The product, however, contained considerable carbonaceous material (MP Ames 3). Recently it has been found that UF_6 can be reduced to UF_4 with propane, using a torch to carry out the reaction (SAM-Carbon and Carbide 6). A mixture of hydrogen and arsine fails to reduce UF_6 at room temperature.

UF_6 reacts with hydrogen chloride at 200°C and much more rapidly at 250°C or 300°C (MP Ames 4). At 200°C, a mixture of brown, green and black products was obtained which, when degassed in vacuum, became green (compare U_2F_9, U_4F_{17}). Material from the 250°C experiment was predominantly brown, with some green and black product also present. The reaction is best carried out in an all-nickel apparatus. The UF_6 vapor is swept in a stream of nitrogen into the chamber where it is brought into contact with hydrogen chloride just inside the chamber at a temperature of 225°C. The reaction product consists of white and blue needles which rapidly change to green in air, and which must be heated in vacuum to obtain pure UF_4. This is probably the best method for reducing UF_6 to UF_4.

With hydrogen bromide the reaction proceeds smoothly at 80°C giving a light green, fluffy powder. Analysis showed the presence of oxyfluoride, a contamination which was attributed to the water content of the bromine used in preparing the hydrogen bromide.

The following thermodynamic estimates were made for the reduction of UF_6 by hydrogen and the two hydrogen halides (at 25°C):

$$(68)\quad UF_{6(s)} + H_{2(g)} \longrightarrow UF_{4(s)} + 2HF_{(g)} \qquad (\Delta F^{o} = -68{,}900 \text{ cal})$$

$$(69)\quad UF_{6(s)} + 2HBr_{(g)} \longrightarrow UF_{4(s)} + 2HF_{(g)} + Br_2 \qquad (\Delta F^{o} = -43{,}500 \text{ cal})$$

$$(70)\quad UF_{6(s)} + 2HCl \longrightarrow UF_{4(s)} + 2HF_{(g)} + Cl_{2(g)} \qquad (\Delta F^{o} = -23{,}400 \text{ cal})$$

Reduction of UF_6 with hydrogen must have a particularly high activation energy, since this reaction is by no means fast even at 600°C, whereas the other two reactions proceed much more readily.

The Ames group has studied the reduction of UF_6 by ammonia (MP Ames 5). Gaseous ammonia reacts with UF_6 at dry ice temperature. The reaction has also been carried out in the gas phase at 300°C in a nickel reactor. The product obtained in this way is not pure UF_4. X-ray studies showed the presence of ammonium fluoride. Some new, unidentified lines were also present, but there were no lines due to UF_4. Chemical analysis indicated the presence of a double salt corresponding to a mixture of 2 per cent NH_4F and 98 per cent NH_4UF_5.

Experiments in which UF_4 was fused with an excess of acid ammonium fluoride at 450°C until all the HF was expelled yielded a product which had an x-ray pattern practically indistinguishable from the reaction product of UF_6 and NH_3. Analytically, also, the products were practically identical, differing only in ammonium fluoride content. The x-ray diagram indicates the arrangement of uranium atoms in this double saltto be very different from that in UF_4.

The liquid phase reduction of UF_6 by $SiCl_4$, $SOCl_2$, and PCl_3 has recently been studied. All of these reagents reduce UF_6 at room temperature, and thionyl chloride apparently gives a quantitative yield of UF_4 (CEW-TEC 5).

Amorphous carbon reduces UF_6 to UF_4 on heating, with the formation of CF_4 and other fluorination hydrocarbons. Silicon, on heating, yields SiF_4, while arsenic yields AsF_3. Phosphorus reacts like silicon, and on moderate heating gives PF_3. UF_6 also reacts with sulfur, giving UF_4, US_2 and a sulfur fluoride gas (m.p. = -135°C, b.p. = -40°C) which is probably SF_4 (Ruff, 1911).

The reaction of UF_6 with mercuric cyanide has been studied in an attempt to prepare volatile uranium compounds containing the -NC group (which is isosteric with CO). UF_6 was distilled on to dry $Hg(CN)_2$ and allowed to react for 24 hours. However, no volatile products other than UF_6 could be detected, and the $Hg(CN)_2$ appeared to be unaffected (British 29).

(e) Effect of Radiation on UF_6 (MP Chicago 3,4). UF_6 undergoes decomposition when bombarded by electrons or deuterons. Gaseous UF_6 (75°C), exposed to 2.2 Mev electrons, (total exposure of 35μa for 120 minutes) gives a voluminous deposit of gray solid. Liquid UF_6 (75°C) when irradiated with 2.7 Mev electrons (35μa) also decomposed to an appreciable extent. There is a marked increase in pressure in a closed system due to the formation of a gas which apparently is free fluorine. Bombardment of UF_6 vapor (75°C) with 6 Mev deuterons at 3μa for 15 minutes causes the formation of a gray solid in amount comparable to that obtained by electron bombardment. At 150°C the phenomena are qualitatively the same as the lower temperatures, but indications are that less decomposition occurs presumably because the back reaction ($UF_5(?) + F_2 \longrightarrow UF_6$) proceeds more rapidly. A blank run showed that the reactions observed at 150°C were due to radiation and not to thermal decomposition (of UF_6) or to attack on the cell.

The results from radiation are similar to those obtained in experiments on the irradiation of UF_6 with ultraviolet light (Columbia 29). Uranium hexafluoride, when exposed to radiation from a G.E. type S-1 sunlamp at 110°C for a few days, deposited a heavy coating of white to yellow dust. A permanent gas was formed which, from its vapor pressure and reactivity toward mercury, appeared to be free fluorine. Lack of data prevents a more extended discussion.

(f) Reduction of UF_6 by Metals. These reactions are discussed in detail in Section 3.3a on the corrosion behavior of UF_6.

3.2 Solutions of Uranium Hexafluoride in Various Solvents.

(a) Miscellaneous Organic Compounds (Ruff, 1911; Columbia 6) Uranium hexafluoride dissolves in a number of organic solvents to form practically perfect solutions. Since UF_6 is a strong fluorinating agent, it reacts with most organic compounds to give hydrogen fluoride and carbon fluorides. Solutions in some chlorinated hydrocarbons, however, are quite stable for periods up to several weeks. Recently, completely fluorinated hydrocarbons have been synthesized which are absolutely inert to UF_6, and a considerable amount of solubility data in such solvents has been obtained at the SAM Carbide and Carbon Laboratories and at Columbia University.

Alcohol and ether react rapidly at room temperature with UF_6 to give HF, UO_2F_2, and carbonaceous material. Benzene, toluene and xylene also react rapidly. UF_6 dissolves in nitrobenzene to give a dark red solution which fumes in air. Paraffin hydrocarbons (i.e., n-cetane, $C_{16}H_{34}$) do not dissolve UF_6, but react rapidly at room temperatures with evolution of hydrogen fluoride and carbonization. Oils containing unsaturated hydrocarbons react more rapidly. UF_6 is insoluble in carbon disulfide. With dry CS_2 a slow reaction takes place; with moist CS_2, sulfur fluorides, very similar if not identical with those obtained by the action of UF_6 on sulfur, are formed.

(b) Halogenated hydrocarbons (Ruff, 1911; Columbia 6). UF_6 is soluble in carbon tetrachloride, chloroform and symmetrical tetrachloroethane. Of these s- tetrachloroethane, $Cl_2CHCHCl_2$, forms the most stable solution, extensive reaction occuring only after several days at room temperature. On boiling, the yellow solution of UF_6 in $C_2H_2Cl_4$ becomes colorless; it regains its yellow color on cooling, indicating that the color may be due to complex formation. Some reactions of UF_6 - $C_2H_2Cl_4$ solutions have been examined. Nitric oxide, NO, colors such solutions blue-green; gaseous ammonia forms a green color, with the simultaneous separation of a flaky material containing fluorine, ammonium and tetravalent uranium. This substance is easily soluble in dilute sulfuric acid, thus differing from UF_4. Its composition is unknown. Arsenic trichloride precipitates a rust-brown solid soluble in excess reagent. These reactions of dissolved UF_6 merit more detailed study. Pentachloroethane, CCl_3CCl_2H, also forms a yellow UF_6 solution which becomes colorless on boiling. This solution deposits good crystals of UF_6 on cooling. Solutions in this solvent are more stable than those in tetrachloroethane, with only a small amount of decomposition occuring after several weeks. 1,2 difluoro-1,1,2,2, tetrachloroethane, FCl_2CCCl_2F, reacts rather rapidly with UF_6. Gas evolution occurs (probably CCl_2F_2), and ultimately all of the UF_6 is reduced to UF_4. Trichloroethylene, $Cl_2C = CClH$, reacts immediately to form UF_4.

(c) Fluorocarbons. The completely fluorinated hydrocarbons are extremely inert to most reagents. The only reagent known to react with them at ordinary temperatures is fluorine, which reacts to form CF_4. Metallic sodium or potassium react above 400°C. The thermal stability of the fluorocarbons is high; temperatures of 400°-500°C do not affect them. Nitric acid (96 per cent), fuming sulfuric acid, acid chromate, or permanganate solution are without effect; bromine and iodine do not react although hydrogen (100 atmospheres, 450°C) removes some fluorine as hydrogen fluoride. Dilute or concenrated alkalis do not affect the fluorocarbons up to 100°C. The liquid, saturated fluorocarbons are insoluble in water, alcohols and hydrocarbons, but show appreciable solubility, and at higher temperatures, complete miscibility, with chlorinated hydrocarbons. The fluorocarbons are completely miscible with ethyl ether and with partly fluorinated hydrocarbons such as benzotrifluoride, $C_6H_5 \cdot CF_3$. For details of the preparation and other properties of these interesting compounds, the reader is referred to other volumes of this series. The physical properties of a few fluorocarbons are given in Table 27.

TABLE 27

PHYSICAL PROPERTIES OF SOME FLUOROCARBONS

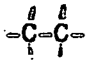
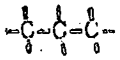
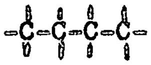
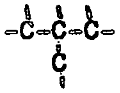
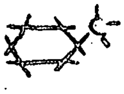
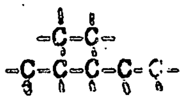
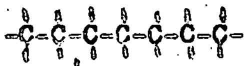
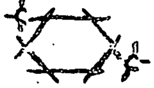
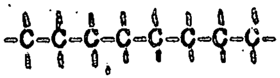
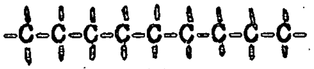
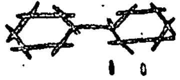
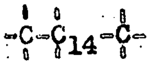
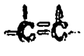
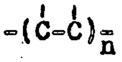
Empirical Formula	Carbon Skeleton	M.P. (°C)	B.P. (°C)	n_D^{20} (liq.)
CF_4		-183.5	-128.0	
C_2F_6		-100.6	- 78.2	
C_3F_8		-183	- 38	
C_4F_{10}	 or 	(-85)	3.0	
C_5F_{10}		-12	22	1.245
C_6F_{12}		50	52	1.2725
C_7F_{14}			76	1.275
C_7F_{16}			83	1.267
C_7F_{16}		-60	82.2	1.2587
C_8F_{16}			100.	1.291
C_8F_{18}			104	1.284
C_9F_{18}			123	1.298
C_9F_{20}			123	1.283
$C_{10}F_{18}$		-75	138	1.314
$C_{12}F_{22}$		75	90(90 mm)	
$C_{16}F_{34}$		114	240	
C_2F_4		-78.4		
$(C_2F_4)_4$		white insoluble, infusible solid		

TABLE 27

PHYSICAL PROPERTIES OF SOME FLUOROCARBONS

d_{20} (liq.)	Vapor Pressure $\log_{10}P = \frac{A}{T} + B$		Latent Heat of Vapor. at B.P (cal.)	Surface Tension at 20°C	Viscosity of Liq. at 20°C (millipoises)
	A	B			
1.91(-183°)	701.73	5.0442	2947		
1.70(-100)	875.7	7.376	4004		
1.45(0.2°C)	1070	7.43	4920		
1.53(0.2°C)	1260	7.44	5800		
1.67	1350	7.43	6200		
1.714	1500	7.51	6900		
1.789					
1.730					
1.721	1660	7.51	7550	13.2	9.9
1.85					
1.73				15.7	16.3
1.89					26.1
1.80				15.5	20
1.92				19.25	56.2

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Solutions of UF_6 in fluorocarbons are extremely stable. Reduction, which is occasionally observed, is usually attributable to reaction with the container or to small amounts of hydrofluorocarbons which may be present in the solvent. Pure fluorocarbons ($C_6F_{12}C_7F_{16}$) show no reaction at 95°C after several hundred hours (Columbia 30). Gaseous UF_6 does not react with n-C_7H_{16} at 300°C, although both compounds begin to show signs of decomposition at higher temperatures.

To a first approximation Raoult's Law is obeyed in UF_6-fluorocarbon systems. Solubilities may therefore be derived on the basis of Raoult's Law and vapor pressure data for uranium hexafluoride. At any temperature below the triple point (64.05°C), the solubility of UF_6 will be directly proportional to the vapor pressure of the solid at that temperature. Employing the vapor pressure data for liquid UF_6 embodied in equation (32), equation (71) can be obtained which gives the solubility, N, of $UF_{6(g)}$ in terms of its partial pressure over the solution:

$$(71) \quad \log N_1 = \frac{1505.9}{T} - 7.5223 \quad \log \rho_{\text{mmHg}}$$

where ρ_{mm} = partial pressure of UF_6 above the solution

N_1 = mole fraction of UF_6 in the solution

T = temperature in °K

This equation is applicable up to the critical temperature if Raoult's Law is obeyed.

For temperatures below 64.05°C, equation (71) is still applicable. It is necessary, however, to use "extrapolated liquid vapor pressures." As the partial pressure of the solute, UF_6, is raised, it will reach the vapor pressure of the pure solid before attaining that of the "extrapolated liquid" below 64.05°C; as soon as a solid UF_6 phase appears, solubility will be at its maximum. The ratio of solid to "extrapolated liquid" vapor pressures will express this point of maximum solubility, and using the data for UF_6 vapor pressure given in equations (26) and (32), the solubility of $UF_{6(s)}$ is given by:

$$N_1 = P_1^s / P_1^L \qquad (72\ a)$$

$$\log N_1 = \frac{1117.4}{T} + 3.3184 \qquad (72\ b)$$

P_1^s = vapor pressure of $UF_{6(s)}$ at T

P_1^L = vapor pressure of $UF_{6(l)}$ at T

N_1 = mole fraction UF_6 in solution

T = temperature in °K

This discussion of perfect solutions is based on that of W. R. Libby (Columbia 31).

Raoult's Law calculations, as given above, are adequate for many purposes. However, many of the systems examined show deviations of 10 to 100 per cent from the Raoult Law calculations. The deviations are positive, i.e., low solubility, especially for low values of N_{UF_6}. In Table 28, 29, 30, 31 and 32 and 32a are given experimental values of the solubility of $UF_{6(g)}$ and $UF_{6(s)}$ in three fluorocarbons. The activity coefficient, γ, for UF_6 is defined as:

(73) $\gamma_1 = \frac{a_1}{N_1}$

γ_1 = activity coefficient

N_1 = observed mole fraction of UF_6 in solution

a_1 = f/f_o which is taken as equal to P/P_o, or Raoult's mole fraction

Where $\gamma > 1$, a positive deviation of $100\ (\gamma - 1)$ per cent from Raoult's Law is indicated. The data embodied in the tables was obtained at Columbia.

TABLE 28*

SOLUBILITY OF GASEOUS URANIUM HEXAFLUORIDE IN PERFLUORO-ISOPROPYL ETHER $(C_3F_7)_2O$

T°C	Total P mm	P_{UF_6}(mm)**	g UF_6 per 100 g Solvent	N_{UF_6}	Raoult N_{UF_6}	γ_{UF_6}
0	110.1	10.1	6.9	0.065	0.122	1.88
10.0	175.5	24.5	11.7	0.105	0.188	1.79
20.0	271.0	57.0	19.7	0.165	0.262	1.59
30.0	406.7	96.7	21.2	0.176	0.292	1.65
	423.5	139	33.0	0.249	0.524	2.10
40.0	594.4	149	21.42	0.176	0.269	1.53
	626.5	243	41.2	0.293	0.487	1.66
50.0	848.5	221	21.2	0.176	0.314	1.78
	904.8	367	41.3	0.293	0.520	1.78

* (Columbia 32).
** assuming γ ether = 1

TABLE 29*

SOLUBILITY OF SOLID URANIUM HEXAFLUORIDE IN PERFLUORO-ISOPROPYL ETHER $(C_3F_7)_2O$

T°C	N_{UF_6}	Raoult N_{UF_6}	γ_{UF_6}
0	0.0645	0.21	3.26
10	0.102	0.31	3.04
20	0.159	0.37	2.33
30	0.246	0.46	1.87
40	0.356	0.58	1.63
50	0.514	0.76	1.78

Deviations from Raoult's Law for the $UF_6-(C_3F_7)_2O$ system are shown graphically in Figure 10. Figure 11 shows some vapor pressure - temperature curves for the same system.

*(Columbia 32)

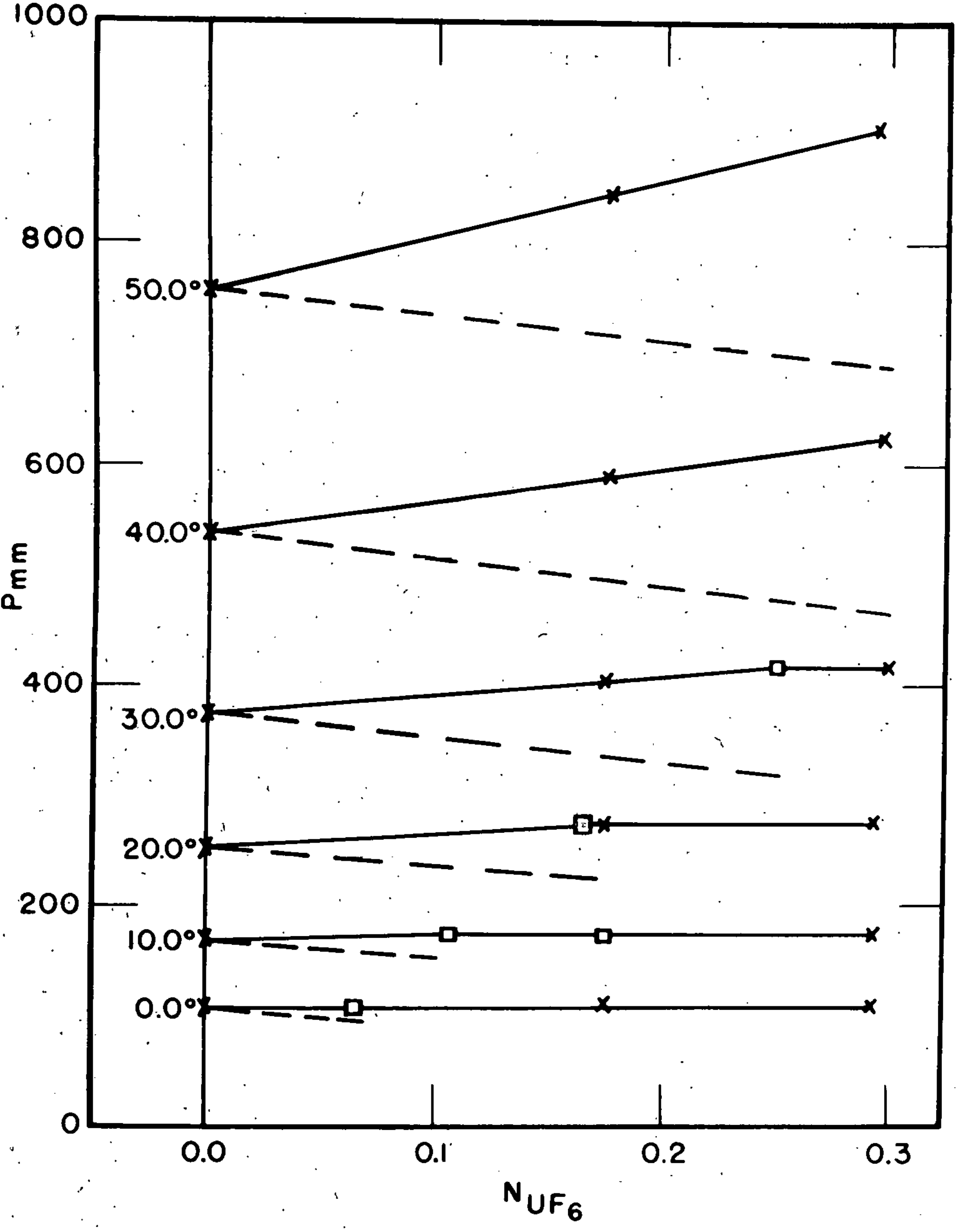
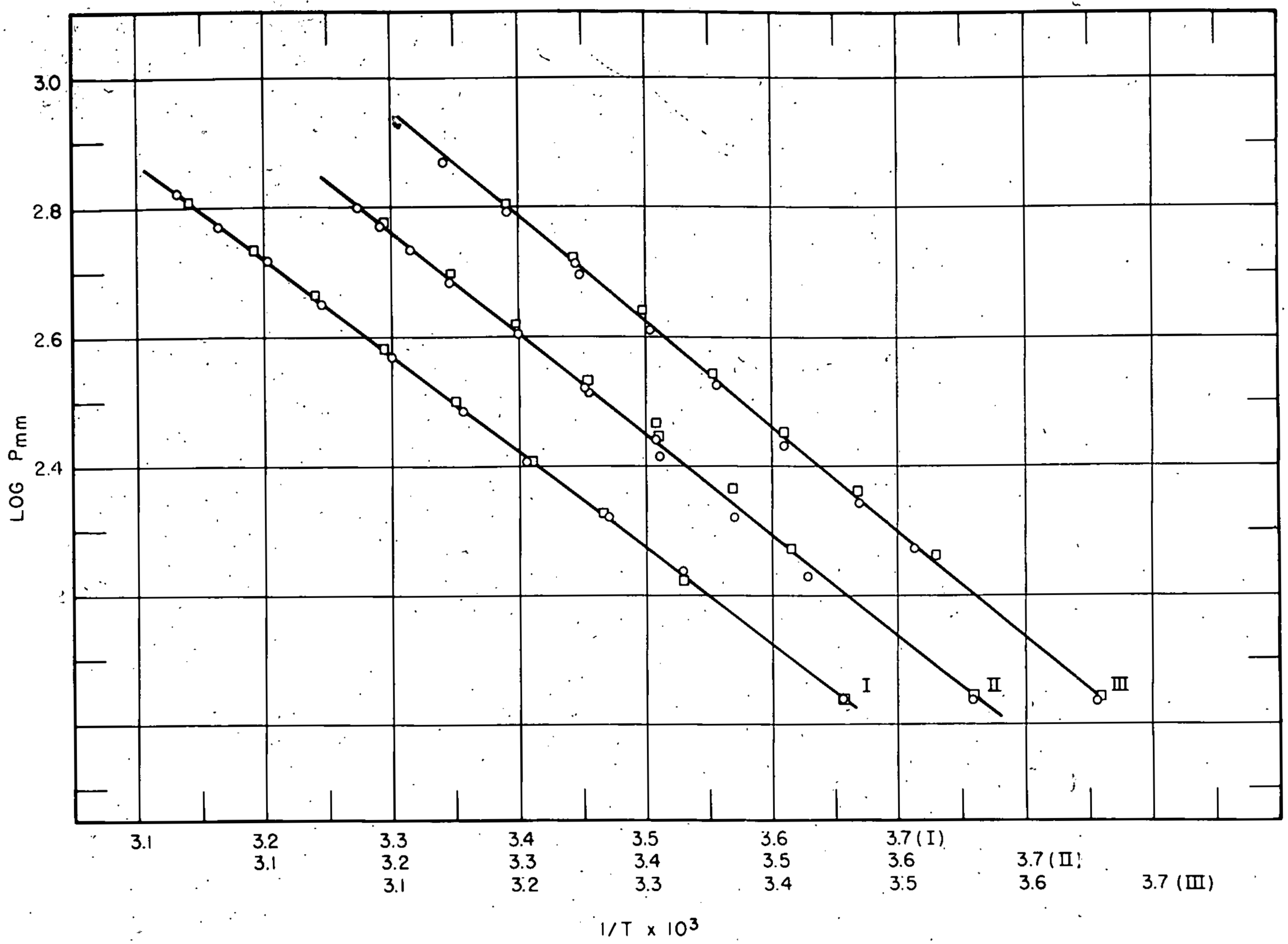


FIG. 10. URANIUM HEXAFLUORIDE – PERFLUORO-ISOPROPYL ETHER SYSTEM.

- – – – RAOULT'S LAW
- □ CONCENTRATION CALCULATED FROM SOLUBILITY MEASUREMENT AT WHICH SATURATION WAS REACHED.
- x EXPERIMENTAL DATA



G. 11 VAPOR PRESSURE OF PERFLUORO-ISOPROPYL ETHER-URANIUM HEXAFLUORIDE SYSTEM.

○ ASCENDING TEMPERATURE
□ DESCENDING TEMPERATURE

I = PURE ETHER. $LOG_{10} P_{mm} = -1492/T + 7.498$
II = 17.6 MOLE % UF_6. $LOG_{10} P_{mm} = -1566/T + 7.774$
III = 29.3 MOLE % UF_6. $LOG_{10} P_{mm} = -1615/T + 7.954$

TABLE 30*

SOLUBILITY OF GASEOUS URANIUM HEXAFLUORIDE IN PERFLUORO-n-HEPTANE, C_7F_{16}

T°C	$P_{UF_6 (mm)}$**	g UF_6/100 g Solvent	N_{UF_6}	Raoult N_{UF_6}	γ_{UF_6}	$\gamma_{C_7F_{16}}$
103.8	104	1.38	0.0150	0.342	2.28	0.99
101.8	204	3.74	0.0395	0.0695	1.76	1.00
101.0	248	4.66	0.0489	0.0850	1.74	1.00
99.1	353	7.33	0.0747	0.125	1.68	1.00
98.7	366	7.36	0.0759	0.131	1.72	1.01
82.8	1078	73.9	0.449	0.557	1.24	1.04
80.8	1162	106	0.561	0.640	1.14	1.14
78.9	1250	169	0.651	0.690	1.06	1.18
78.0	1295	238	0.724	0.739	1.02	1.26
77.2	1335	283	0.757	0.789	1.04	1.20
76.4	1382	363	0.800	0.834	1.04	1.12
75.8	1404	476	0.840	0.865	1.03	1.20
75.2	1415	977	0.915	0.888	0.97	2.08
73.8	1508	-	0.978	0.990	1.01	0.98
73.6	1520	-	1.000	1.000	1.00	-

* (Columbia 33).

** Total pressure maintained at 1520 mm Hg.

TABLE 31*

SOLUBILITY OF SOLID URANIUM HEXAFLUORIDE IN PERFLUORO-n-HEPTANE C_7F_{16}

T°C	Total Pmm	g UF_6/100 g Solvent	N_{UF_6}	Raoult N_{UF_6}	γ_{UF_6}**
-7.8	22	10.0	0.10	0.14	1.40
18.3	109	22.7	0.20	0.36	1.80
33.9	248	38.9	0.30	0.52	1.72
40.6	362	60.2	0.40	0.63	1.58
46.1	465	90.7	0.50	0.69	1.39
51.7	620	136.	0.60	0.77	1.29
55.0	725	212.	0.70	0.84	1.19
58.9	880	363.	0.80	0.91	1.13
61.1	1010	-	0.90	0.95	1.05

* (Kellex 1).

** Assuming $\gamma_{C_7F_{16}} = 1$

TABLE 32

SOLUBILITY* OF GASEOUS URANIUM HEXAFLUORIDE IN PERFLUORO-DIMETHYL CYCLOHEXANE, C_8F_{16}

T°C	Total P mm	g UF_6/100 g Solvent	N_{UF_6} (solution)	N_{UF_6} (vapor)	γ_{UF_6}	$\gamma_{C_8F_{16}}$
20	59	9.7	0.10	0.50	1.40	1.07
30	91	9.7	0.10	0.48	1.24	1.05
	135	21.8	0.20	0.70	1.35	1.02
40	135	9.7	0.10	0.47	1.29	1.03
	202	21.8	0.20	0.68	1.40	1.04
	238	37.4	0.30	0.73	1.18	1.18
60	305	9.7	0.10	0.45	1.37	1.02
	425	21.8	0.20	0.66	1.40	0.99
	605	58.3	0.40	0.80	1.21	1.10
	735	131.	0.60	0.89	1.09	1.10
80	615	9.7	0.10	0.41	1.40	1.07
	828	21.8	0.20	0.62	1.42	1.04
	1140	58.3	0.40	0.79	1.25	1.04
	1370	131.	0.60	0.89	1.13	1.00
	1600	349.	0.80	0.93	1.03	1.48
100	1090	9.7	0.10	0.40	1.45	1.02
	1450	21.8	0.20	0.60	1.45	1.02
	1960	58.3	0.40	0.78	1.28	1.01
	2380	131.	0.60	0.88	1.16	1.01
	2690	349.	0.80	0.92	1.03	1.52
150	3780	9.7	0.10	0.36	1.68	1.02
	4750	21.8	0.20	0.58	1.70	0.95
	6200	58.3	0.40	0.74	1.42	1.02
	7250	131.	0.60	0.82	1.22	1.23
	8380	349.	0.80	0.90	1.15	1.57

* Solubility data are probably accurate to about 5%.

TABLE 32*

SOLUBILITY** OF SOLID URANIUM HEXAFLUORIDE IN PERFLUORO-DIMETHYL CYCLOHEXANE, C_8F_{16}

T^oC	Total P mm	g UF_6/100g Solvent	N_{UF_6}	Raoult N_{UF_6}	γ_{UF_6}
-2.2	17	9.7	0.10	0.19	1.9
21.1	93	21.8	0.20	0.38	1.9
27.8	197	37.4	0.30	0.45	1.5
41.6	310	58.3	0.40	0.62	1.5
47.8	465	87.3	0.50	0.73	1.4
52.2	595	131.	0.60	0.79	1.3
56.1	725	204.	0.70	0.86	1.2
58.9	880	349.	0.80	0.92	1.2
61.6	1030	785.	0.90	0.96	1.1

* (Kellex 1).
** Solubility data is probably accurate to within ± 2%.

(d) Solutions of UF_6 in Inorganic Solvents. The qualitative behavior of uranium hexafluoride with a large number of inorganic "solvents" has been studied at the SAM Laboratories of Columbia University (Columbia 32). Quantitative data have been obtained for the UF_6 - HF, and UF_6 - BF_3 systems.

The $UF_{6(l)}$ - HF system exhibits extreme deviation from Raoult's Law (Columbia 32). The vapor pressure curves for this system are given in Figure 12. The system breaks down into phases in the middle concentration range as does the phenol-water system. At

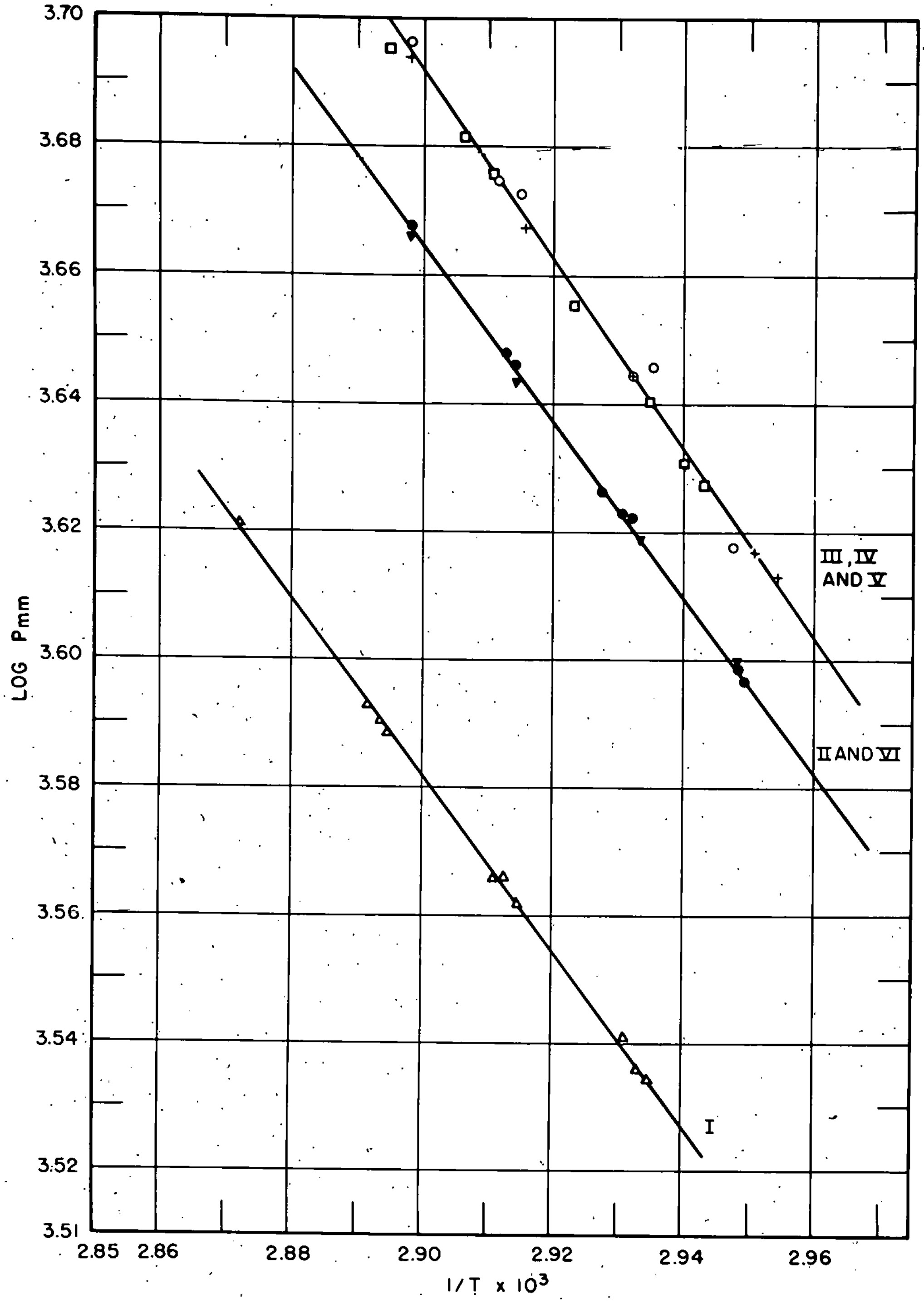


FIG. 12. VAPOR PRESSURE OF HYDROGEN FLUORIDE – URANIUM HEXAFLUORIDE SYSTEM.

I Δ = PURE HF III ○ = 9.01 MOLE % UF_6 V □ = 71.6 MOLE % UF_6
II ● = 3.84 MOLE % UF_6 IV + =>14.1 MOLE % UF_6 VI ▼ = 83.5 MOLE % UF_6
ASSUMING MOL. WT. OF HF = 20
I $\mathrm{LOG}_{10} P_{mm} = -1375/T + 7.5697$ II AND VI $\mathrm{LOG}_{10} P_{mm} = -1375/T + 7.6519$
III, IV AND V $\mathrm{LOG}_{10} P_{mm} = -1471/T + 7.9578$

68°C and 4410 mm Hg pressure, two phases exist between $N_{UF_6} = 0.05$ and 0.825. Solubilities for the one-phase system are given in Table 33, and the UF_6 - HF vapor pressure composition curve is given in Figure 13.

TABLE 33

SOLUBILITY OF HYDROGEN FLUORIDE IN LIQUID URANIUM HEXAFLUORIDE

T°C	Total P mm	P^*_{HF} mm	g HF/100g UF_6	N_{UF_6}	N_{HF}	γ HF
68	4180	4131	137	0.038	0.962	1.25
	4180	3130	1.1	0.835	0.165	5.50
70	4410	4359	137	0.038	0.962	1.24
	4410	3280	1.1	0.835	0.165	5.45
72	4650	4595	137	0.038	0.962	1.24
	4650	3440	1.1	0.835	0.165	5.41

* Assuming $\gamma_{UF_6} = 1$.

The melting point-composition diagram for the UF_6-BF_3 system, Figure 14, has also been worked out at Columbia (34). UF_6 is only very sparingly soluble in BF_3 at about -125°C.

3.3 <u>Reactions of UF_6 with Metals and Other Materials of Construction</u>. Uranium Hexafluoride, reacts with most metals or other common materials of construction. The problem of finding inert materials has therefore received a great deal of attention.

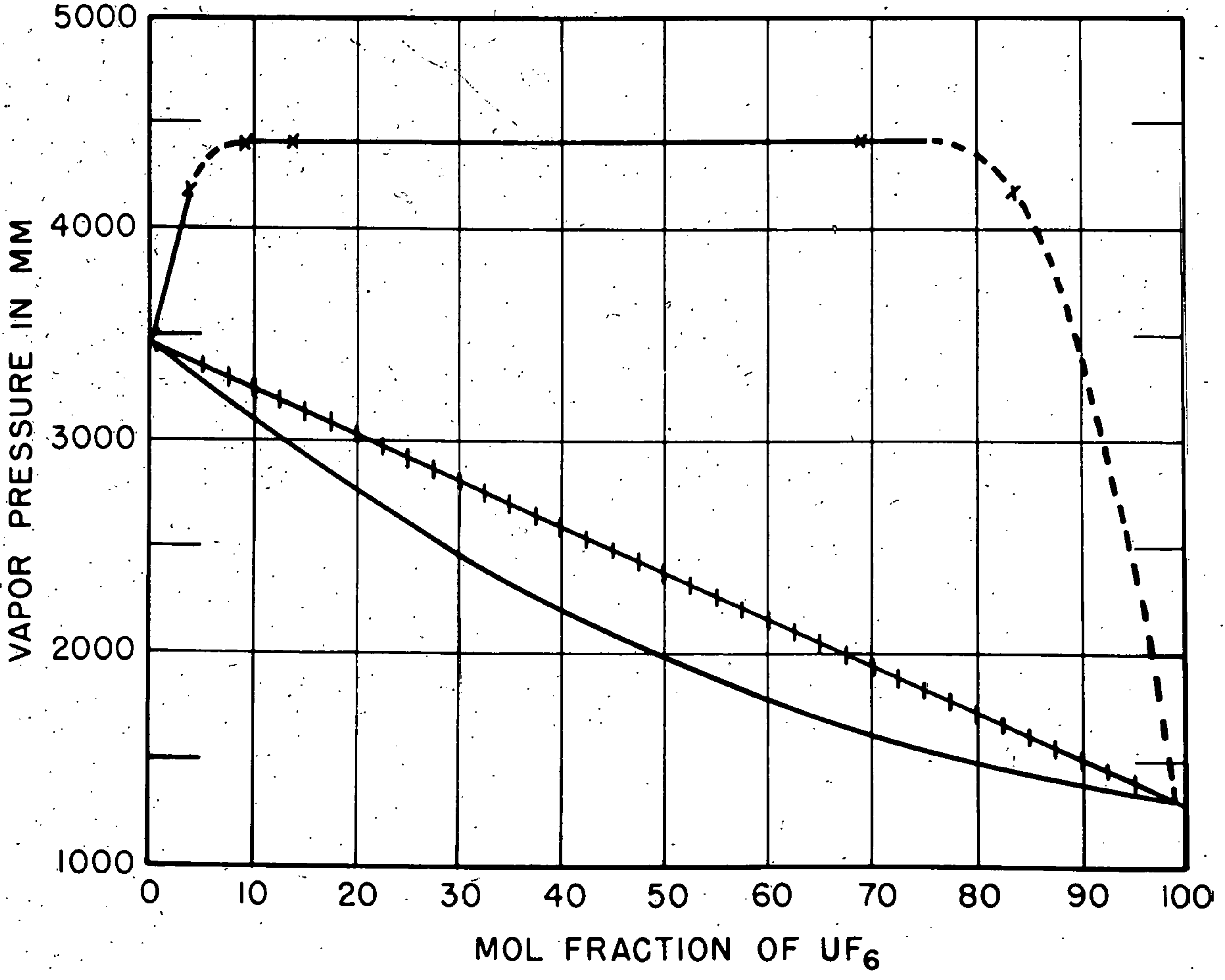


FIG. 13. VAPOR PRESSURE OF HYDROGEN FLUORIDE-URANIUM HEXAFLUORIDE SYSTEM AT 68°C.

- - - UNCERTAIN EXTRAPOLATION
—— RAOULT'S LAW (ASSUMING MOL. WT. OF HF = 40)
—+++— RAOULT'S LAW (ASSUMING MOL. WT. OF HF = 20)
x EXPERIMENTAL DATA

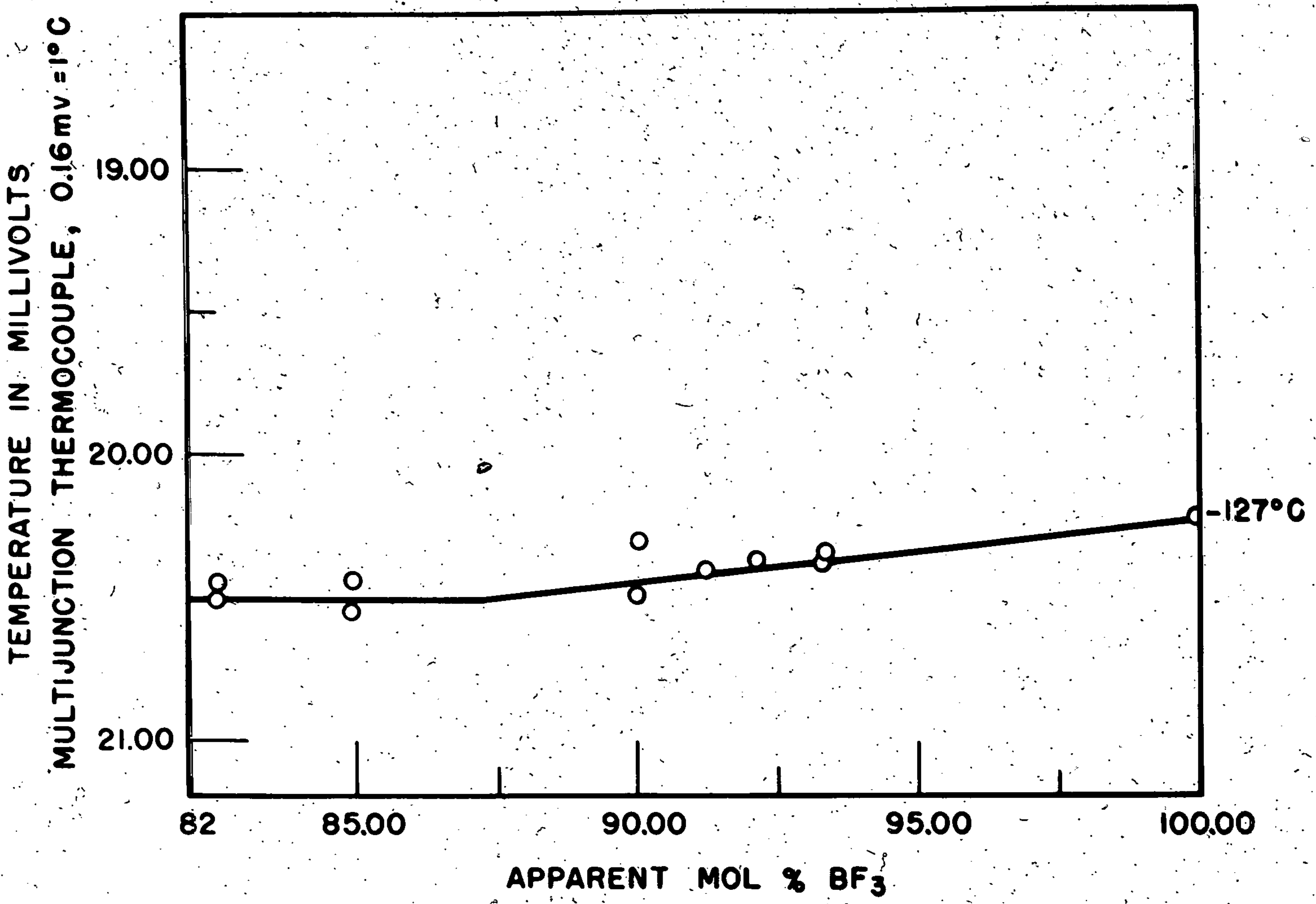


FIG. 14. MELTING POINT DIAGRAM OF THE BORON TRIFLUORIDE–URANIUM HEXAFLUORIDE SYSTEM.
○ EXPERIMENTAL DATA

(a) Metals and Alloys. A variety of methods have been employed in evaluating the corrosion resistance of various materials. Ruff and Heinzelmann (1911) made a number of qualitative observations by exposing various substances to UF_6 vapor. Gold and platinum were reported to show no reaction in the cold, but tarnished slightly on heating. Mercury reacted in the cold. Copper and silver showed slight attack on warming. Lead, tin, zinc and iron reacted more vigorously than copper or silver. Aluminum was covered with a white coating. Sodium reacted rapidly, catching fire when warmed with UF_6.

An exhaustive series of investigations has been carried out at Columbia in an effort to find suitable materials of construction. Pure metals, a very large number of alloys, and various organic coatings and elastomers were examined by a so-called static method (Columbia 35,36). Samples were placed in a pyrex tube, outgassed thoroughly, and enough UF_6 admitted to ensure the presence of saturated vapor at the temperature of the test. The tubes were then sealed off and heated to the desired temperatures for long periods. The degree of stability of the material was estimated after the test by visual observation of its appearance, weighing, and other semi-quantitative methods. The results are summarized in Tables 34 and 35. British workers have carried out similar experiments with substantially the same results (British 30). The only really significant difference of opinion occurs in the question of the utility of steel.

Metal	Pretreatment	Conditions of Exposure		Observations	Conditions Under Which the Material May be Used	Ref.
		Temp. (°C)	Time (days)			
Aluminum		160	5	Little attack. No weight change.	Satisfactory for most uses.	(a)
Beryllium	Cleaned with CCl_4	90	4	Some pitting, but only a rather superficial attack.	Satisfactory when exposure time is limited to one month or less.	(b)
Bismuth	Cleaned with toluene	80	4	Some evidence of attack. Sample crumbled after treatment.	Unsatisfactory for use with UF_6.	(b)
Cadmium		65	3	Badly etched and blistered.	Unsuitable under any conditions.	(a)
Copper	Cleaned with HNO_3	160	7	No loss in weight and little attack.	Almost as satisfactory as Ni. Suitable under any conditions.	(a)
Gold					Should not be used above 75°C, pref. not at all.	(a)
Indium	Cleaned with CCl_4	90	4	Surface shows	Unsuitable under any conditions.	(b)
Lead	Cleaned and one side polished	150	7	Sample dulled and pitted. All UF_6 decomposed.	Unsuitable under any conditions.	(a)

TABLE 34
CORROSION RESISTANCE OF PURE METALS IN URANIUM HEXAFLUORIDE VAPOR

(cont'd)

Metal	Pretreatment	Conditions of Exposure		Observations	Conditions Under Which The Material May Be Used	Ref.
		Temp. (°C)	Time (days)			
Magnesium	Machined and cleaned with toluene	190	7	Appreciable amount of adherent green scale.	Suitable for use under all conditions.	(b)
Manganese	Electrolytic metal	75	56	Some loss in luster. No weight loss or attack.	Should be satisfactory as alloying material.	(a)
Nickel	Cleaned and polished	160	10	Slightly dulled after treatment.	Best material. Suitable for any conditions.	(a)
Palladium	Foil	75	28	No indication of attack.	Probably satisfactory at 75°C. Attacked at high temps. (400°	(a)
Platinum					Same as for Pd.	(a)
Silver	Massive Metal	75	30	Slight deposit. A few black spots. No loss in weight.	Should not be used above 75°C, preferably not at all.	(a)
Tantalum		20-70	10	No attack(?)	(?)	(c)
Tin	Cleaned and polished	75	30	Attack. Fairly heavy deposit.	Should not be used above 75°C; preferably not at all.	(a)
Zinc	Cleaned and filed	75	30	Heavy deposit. Etch patterns. No loss in weight.	Should not be used above 75°C; preferably not at all.	(a)

(a) (Columbia 35). (c) (Britich 20).

(b) (Columbia 36).

Table 34 (continued)

Alloy	Pretreatment	Conditions of Exposure		Observations	Conditions Under Which the Material May Be Used	Ref
		Temp. (°C)	Time (days)			
Cast Dow Metal H19721	Cleaned with toluene; one surface machined.	80	5	No apparent effect.	Satisfactory for use with UF_6.	(a)
95-5 Aluminum Brass	Cleaned with toluene; polished on outside.	90	4	No apparent effect.	Satisfactory for use with UF_6.	(a)
Nichrome	Cleaned with toluene.	125	7	Showed very little attack.	Satisfactory provided only small surfaces are exposed.	(a)
Bearing Bronze 90-5-5	Cleaned mechanically and washed with toluene.	75	4	Definite coating of abrasive green material.	In general unsatisfactory except perhaps under unusually mild conditions.	(a)
Tin Babbit Metal	Cleaned by degreasing followed by acid pickle.	100	4	Coating of greenish material.	Not satisfactory for use with UF_6.	(a)

TABLE 35
CORROSION RESISTANCE OF SOME ALLOYS IN URANIUM HEXAFLUORIDE VAPOR
(continued)

TABLE 35 (Continued)

Alloy	Pretreatment	Conditions of Exposure		Observations	Conditions Under Which the Material May Be Used	Ref
		Temp. (°C)	Time (days)			
Phosphor Bronze	Polished	75	30	White adherent deposit; pronounced etching but no weight loss.	Quite resistant to UF_6 at 75°C.	(a)
Beryllium Copper	Polished	75	40	Slightly colored, practically no deposit on etching.	Very resistant at 75°C.	(b)
Duralumin 14ST	Polished	160	5	No weight loss and very slight attack.	Satisfactory below 125°C.	(b)
18-8 EZ Stainless Steel	Polished	160	5	Large weight loss; pitting, badly attacked.	Unsatisfactory.	(b)

(a) (Columbia 36).
(b) (Columbia 35).

Tables 34 and 35 may be interpreted as indicating that nickel, copper, and aluminum, in that order, are the most resistant metals. Copper is probably superior to aluminum for piping owing to the ease with which it can be made vacuum tight. These three metals are by far superior to all the others. In general, alloys also are satisfactory if they have a high content of nickel, copper. or aluminum. Materials which form volatile fluorides or which readily exist in a number of different valence states are in general unsuitable for use with UF_6. It must be emphasized that these results are valid only for very pure UF_6. In the presence of even small amounts of hydrogen fluoride, corrosion is much more serious.

Plated surfaces also have received some study (Columbia 35, 37). In general, plating does not afford sufficient protection. For example, cadmium plate gave no protection to steel ~~shell~~. Chromium appeared satisfactory up to a temperature of 130°C, but at this temperature the sample was coated with a heavy hygroscopic deposit, which, when removed, also removed a considerable part of the plate. At 160°C, chromium plate was very ineffective. Gold and silver plates do not offer much protection. Copper plate offers little protection. Nickel plates of various types were far superior to any other tried. The British workers consider nickel plate on a copper undercoat to afford "complete" protection to steel.

Although a difference of opinion exists with respect to the corrosion resistance of steels, it appears certain that direct contact of steel with UF_6 at high temperatures should be avoided (Columbia 35). SAE 4140 steel began to lose weight at 75°C, and at 130°C. had lost an appreciable amount indicating serious corrosion. Stainless steel (18.8 EZ 303 and 416) is attacked appreciably at 130°C. and very seriously at 150°C. Stainless steels should probably be avoided. However, British workers find degassed mild steel and cast iron to be quite satisfactory at 70°C. (British 31). The same is true of austenitic steel(18 Ni/8 Cr/1 W/1 Ti). These workers feel that under relatively mild conditions steel would be satisfactory, and that even at 150°C., attack will not be severe enough to affect the mechanical strength of apparatus (British 32).

The corrosion of various metals and alloys in refluxing UF_6 at 110°C. has been studied (MP Chicago 3). The metallographically polished specimens were immersed partly in the vapor and partly in refluxing liquid. Nickel and nickel alloys (Inconel, Monel K, Monel) showed little attack in 257 hours. Beryllium-copper and copper (90%) - tin alloy also showed little attack. Other workers have made static corrosion tests of various metals in contact with liquid UF_6. In general, the results indicate no greater weight changes in liquid UF_6 than in its vapor under the same temperature conditions and time exposure. Metallic uranium was found to corrode at a rate of about 0.2 mg/cm^2/hr at 200°C. in liquid UF_6 (MP Chicago 4).

(b) Corrosion Resistance of Non-Metals. A large number of materials have been examined with a view to their suitability for gaskets, electrical insulation, coatings, etc. None of the materials can be used where there is much exposure to UF_6 especially at elevated temperatures. The British have found that natural rubber is by far the best elastomer available (British 30). Vulcanized unfilled natural rubber is resistant to UF_6 if degassed for eight hours at 100°C., and its physical properties are not affected by exposure to UF_6. The addition of certain fillers such as "blanc fixe" is permissible. These workers find all synthetic rubbers inferior to natural rubber. Butyl rubber causes decomposition unless KF is present in the system. Neoprene, ester rubber, Buna S, and Buna N are not as inert as natural rubber. Polythene and plyisobutylene are found to be reasonably resistant below 100°C; whereas polyvinylchloride, polystyrene, cellulose acetate, polyvinyl acetate, methyl methacrylate, polyvinyl acetal, phenol-formaldehyde and urea-formaldehyde are all attacked by UF_6. Of various insulating materials other than plastics, only mica and pure glass cloth (and possibly silk) are inert. Cellulose (in the form of cotton, wool, or paper), ebonite, asbestos, shellac, wood, and bitumen are all unsuitable for use with UF_6. Priest and Agron (Columbia 36), after examining a large number of samples of butyl rubber and other plastics, concluded that none of them should be used with UF_6 under any condition. Graphite and graphite compounds must be avoided (Columbia 38). Certain varieties of polymerized perfluoro-ethylene show excellent resistance of UF_6 particularly when pretreated.

CHAPTER 13

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CHAPTER 14

URANIUM-CHLORINE COMPOUNDS

1. **Uranium Trichloride**
   - 1.1 Preparation of Uranium Trichloride
   - 1.2 Physical Properties of Uranium Trichloride
   - 1.3 Chemical Properties of Uranium Trichloride

2. **Uranium Tetrachloride**
   - 2.1 Preparation of Uranium Tetrachloride
   - 2.2 Physcial Properties of Uranium Tetrachloride
   - 2.3 Chemical Properties of Uranium Tetrachloride

3. **Uranium Pentachloride**
   - 3.1 Preparation of Uranium Pentachloride
   - 3.2 Physical Properties of Uranium Pentachloride
   - 3.3 Chemical Properties of Uranium Pentachloride

4. **Uranium Hexachloride**
   - 4.1 Preparation of Uranium Hexachloride
   - 4.2 Physical Properties of Uranium Hexachloride
   - 4.3 Chemical Properties of Uranium Hexachloride

CHAPTER 14

URANIUM-CHLORINE COMPOUNDS

Four binary uranium-chlorine compounds are known: UCl_3, UCl_4, UCl_5 and UCl_6. The first three were prepared and studied by the earliest workers in uranium chemistry. The preparation of the fourth, UCl_6, has only recently been effected at the Radiation Laboratory of the University of California. Since this compound and uranium hexafluoride are the only known oxygen-free hexavalent uranium compounds, they are of special interest. Considerable new information on uranium chlorides has been acquired since 1942 , and this material furnishes most of the subject matter of the present chapter.

For convenience, a number of the physical properties of the uranium-chlorine compounds are collected in Table 1.

TABLE 1

SOME PHYSICAL PROPERTIES OF URANIUM-CHLORINE COMPOUNDS

Compound	M.P. (°C)	Density[(a)] (g/cc)	Vapor Pressure $\log P_{mm\,Hg} = A - \frac{B}{T}$		$H_{subl.}$ (kcal/mole)	F^{o}_{298} (kcal/mole)	S_{298} (e.u.)
			A	B			
UCl_3	842±5	5.51	10.0	12000	55.0	-196.2	40.0
UCl_4	590±1	4.87	13.2995	10427	47.7	-229.0	47.14
UCl_5	300(c)	3.81[(b)]	-	-	-	-235.7	57.0[(c)]
UCl_6	177.5[(c)]	3.59	6.634	2422	11.12	-241.4	68.26

(a) From x-ray data.
(b) Direct measurement by immersion in benzene.
(c) These quantities are estimated.

1. Uranium Trichloride

Uranium trichloride was first prepared by reduction of UCl_4 with hydrogen (Peligot, 1842). This is still the most convenient preparative method, particularly if no pure uranium metal is available. The unusual stability of uranium trichloride in air has stimulated considerable interest in the compound.

1.1 Preparation of Uranium Trichloride In addition to the reduction of UCl_4 with hydrogen, uranium trichloride can also be prepared by reaction of uranium hydride with hydrogen chloride. Some other reactions, also leading to UCl_3, are of no practical importance.

(a) UCl_4 + Hydrogen (Brown 1-6; MP Ames 1). The reduction of UCl_4 by hydrogen

$$(1) \qquad UCl_4 + \tfrac{1}{2}H_2 \longrightarrow UCl_3 + HCl,$$

does not proceed rapidly below 500°C. At 525°-550°C the rate is still so slow as to require about five hours for the reaction to go to completion. (See Sec. 2.2d.) It is essential, however, to keep the temperature below 590°C so as to avoid formation of liquid UCl_4, since the molten material easily becomes covered by a layer of UCl_3 which prevents further reduction. It is therefore, advisable to convert most of the UCl_4 to UCl_3 below 575°C; the reduction can then be completed at temperatures up to 650°C. The necessity of using carefully purified hydrogen needs not to be stressed.

Hydrogenation under pressure is much more expeditious (Brown 4,6). Under seven atmospheres at 525°-550°C the reaction proceeds four times as fast as at atmospheric pressure. To prevent sintering the reaction mixture is first kept at 525°C for 30 minutes, and then slowly heated to 550°C. The reaction may be carried out in a stainless steel vessel equipped with vents for exhausting the gases slowly. Uranium tri(?) ~~tetra~~chloride produced in this way is a dark-green crystalline substance.

(b) $UH_3 + HCl$ (MP Ames 2,3). When finely divided uranium metal or uranium hydride is heated with hydrogen chloride at 250°-300°C, olive-green UCl_3 is obtained:

(2) $$UH_3 + 3HCl \longrightarrow UCl_3 + 3H_2$$

The reaction proceeds smoothly and, when metallic uranium is available, this is a very convenient method. A suitable apparatus is that used for preparing UBr_3 (MP Ames 4) (See Chapter 15). Hydrogen chloride is strongly absorbed by the product and can only be removed in vacuum at 150°C.

(c) Miscellaneous Preparations. Uranium tetrachloride can be reduced by ammonia at elevated temperatures, but the product contains nitrogen (Rammelsberg, 1842). Hydrogen iodide may also be used:

(3) $$UCl_4 + HI \xrightarrow{300^\circ-350^\circ C} UCl_3 + HCl + \tfrac{1}{2}I_2$$

In this case the product may be freed from iodine by a stream of dry nitrogen at 200°-300°C (TEC-CEW 1).

It has been observed that UCl_4 vapors react with heated metals according to the equation,

(4) $$xUCl_4 + M \longrightarrow MCl_x + xUCl_3.$$

If the metal, M, forms a volatile chloride, very good yields of crystalline UCl_3 can be obtained. Metallic zinc is particularly suitable (TEC-CEW 2, 32).

When uranium mononitride, UN, is heated in UCl_4 vapor at 500°C for several hours, a product thought to be UCl_3 is obtained. The reacted mass is found to dissolve in water with the evolution of considerable gas and the formation of a purple solution (MP Ames 5). This reaction is of no preparative importance.

Solutions of UCl_3 in concentrated hydrochloric acid are more stable than in pure water, and such solutions can be prepared by electrolytic reduction of a 15 per cent solution of UO_3 in HCl (d = 1.12) (Rosenheim, 1908). The electrolysis is carried out under carbon dioxide in a cell equipped with a porous diaphragm and a mercury cathode. The reduction is performed at 110 volts and 1.5-2.0 amperes with concentrated hydrochloric acid as the anolyte. After the solution, which first rapidly turns green, has acquired a dirty brown-green color, the current is reduced to 0.75-1.0 amp. Further electrolysis is carried out at 0°C with periodic additions of hydrochloric acid until the characteristic red color of uranium(III) is developed. Solutions of uranium(III) can also be prepared by reduction of UO_2Cl_2 with zinc and hydrochloric acid (Zimmerman, 1882).

(d) Purification of UCl_3. Uranium trichloride can be freed from volatile materials (such as UCl_4) by heating to 770°C in vacuum for several hours (Brown 7). An ingenious purification method is based upon the conversion of UCl_3 to UCl_3I by distillation in a stream of iodine vapor:

$$UCl_3 + \tfrac{1}{2}I_2 \longrightarrow UCl_3I. \qquad (5)$$

UCl_3I is volatile; on cooling decomposition to UCl_3 and iodine again occurs. The net result is the distillation of the UCl_3 at temperatures far below those required by its own volatility (UCRL 1).

1.2 Physical Properties of Uranium Trichloride At room temperature UCl_3 is olive-green in color. At 300°C it develops a reddish-brown color, and above 450°, a dark purple color. On cooling to room tempera-

ture, the olive-green color returns. Material prepared by reduction of UCl_4 with H_2 is usually red.

(a) Melting Point (Brown 5, 8). The melting point of UCl_3 is 842° ± 5°C as determined by thermal analysis.

(b) Volatility. The vapor pressure of UCl_3 has been measured by the molecular effusion method. The upper limit of the volatility is in the vicinity of 10^{-2} mm Hg at 820°C and 3.5×10^{-3} mm Hg at 750°C (UCRL 2). An empirical equation has been devised which fits the vapor pressure data in the temperature range 600°-1000°C (UCRL 3).

$$\log P_{\text{mm Hg}} = -\frac{12{,}000}{T} + 10.00 \qquad (6)$$

A heat of sublimation of 55,000 cal/mole is deduced from this equation.

(c) Crystal Structure of UCl_3 (MP Chicago 1). Uranium trichloride has an hexagonal unit cell containing two molecules with the lattice constants:

$$a_1 = 7.428 \pm 0.003 \text{ Å}, \qquad a_3 = 4.312 \pm 0.003 \text{ Å}$$

The space group is $C6_3/m$ ($C6h^2$), and the atomic positions are:

$2\ U$ in $\pm(1/3\ \ 2/3\ \ 1/4)$

$6\ Cl$ in $\pm(x\ y\ 1/4)\ (y-x,\ \bar{x},\ 1/4)\ (\bar{y},\ x-y,\ 1/4)$

with $x = 0.375$, $y = 0.292$

Each metal atom thus has nine halogen neighbors at a distance U-Cl of 2.96 Å. UCl_3 is isomorphous with $CeCl_3$, $LaBr_3$ and $CeBr_3$.

The density of UCl_3 is computed to be 5.51 g/cc from the x-ray data. By direct displacement in CCl_4 a value of 5.35 g/cc was obtained. The density of UCl_3 is therefore higher than that of UCl_4 (MP Ames 1).

(d) Thermochemical Data (Nat. Bur. Standards 1). The specific heat, entropy and enthalpy of UCl_3 have been determined for the temperature range 15°K to 380°K (Nat. Bur. Standards 1) and from 273°K to 1000°K (Nat. Bur. Standards 6). The results are probably accurate to within 1 per cent and are given in Tables 2 and 2A. The values in the latter table are to be preferred.

The heat of formation of UCl_3 has recently been redetermined at UCRL (4) by the method of Biltz and Fendius (1923) (see p.). The result was

$$(7) \qquad U_{(s)} + 3/2\, Cl_{2(g)} \longrightarrow UCl_{3(s)} \qquad \Delta H_{273^\circ} = -212.1 \pm 0.6 \text{ kcal}$$

For details of the calculation we must refer the reader to the original report.

TABLE 2

SPECIFIC HEAT, ENTROPY AND ENTHALPY OF UCl_3 FROM 0° to 380°K

Temp. (°K)	C_p (Int. joules/mole °K)	S (Int. joules/mole °K)	$H-E_0^s$ (Int. joules/mole)
0	0.0	0.0	0.0
5	0.476 (a)	0.159	.597
10	3.15 (a)	1.181	8.73
15	6.64	3.13	33.39
20	9.30	5.43	73.67
25	12.38	7.84	127.8
30	15.51	10.37	197.6
35	18.94	13.01	283.4
40	23.07	15.80	388.1
45	27.2	18.76	513.8
50	31.6	21.85	660.8
55	36.7	25.10	831.6
60	41.8	28.51	1028.
65	46.4	32.04	1248.
70	50.9	35.64	1492.
75	55.2	39.30	1757.
80	59.1	42.99	2043.
85	62.9	46.69	2348.
90	66.6	50.39	2672.
95	70.3	54.10	3014.
100	73.1	57.73	3373.
105	75.4	61.40	3744.
110	77.8	64.96	4128.
115	79.9	68.46	4522.
120	82.1	71.91	4927.
125	84.0	75.30	5342.
130	85.6	78.63	5766.
135	87.2	81.89	6198.
140	88.6	85.09	6638.
145	89.9	88.22	7084.
150	91.2	91.29	7537.
155	92.4	94.30	7996.
160	93.4	97.25	8460.
165	94.3	100.14	8930.
170	95.1	102.97	9403.
175	95.8	105.73	9881.
180	96.4	108.44	10361.
185	97.0	111.09	10845.
190	97.4	113.68	11331.

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TABLE 2 (CONTINUED)

Temp. (^{o}K)	C_p (Int. joules/mole ^{o}K)	S (Int. joules/mole ^{o}K)	$H-E_o$[a] (Int. joules/mole)
195	97.8	116.22	11819.
200	98.1	118.70	12309.
205	98.4	121.12	12800.
210	98.8	123.50	13293.
215	99.2	125.83	13788.
220	99.6	128.11	14285.
225	100.1	130.35	14784.
230	100.5	132.56	15286.
235	100.8	134.72	15789.
240	101.1	136.85	16294.
245	101.4	138.94	16800.
250	101.7	140.49	17308.
255	102.0	143.01	17817.
260	102.2	144.99	18328.
265	102.6	146.94	18839.
270	102.7	148.85	19352.
275	102.8	150.73	19865.
280	102.9	152.58	20379.
285	103	154.40	20893.
290	103	156.19	21408.
295	103	157.95	21923.
298.16	103	159.04	22248.
300	103	159.68	22438.
305	103	161.38	22953.
310	103	163.06	23468.
315	103	164.71	23983.
320	103	166.33	24498.
325	103	167.93	25013.
330	103	169.50	25528.
335	103	171.05	26043.
340	103	172.57	26558.
345	103	174.08	27073.
350	103	175.56	27588.
355	103	177.02	28103.
360	103	178.46	28618.
365	103	179.88	29133.
370	103	181.28	29648.
375	103	182.67	30163.
380	103	184.03	30678.

(a) Extrapolated using Debye Function: 15.665 D $\left(\frac{68.4}{T}\right)$

TABLE 2A

SPECIFIC HEAT, ENTROPY AND ENTHALPY FROM 0°C to 727°C

Temp. (°C)	C_p (Int. joules/mole °C)	S (Int. joules/mole °C)	$H-E_o^s$ (Int. joules/mole)
0	101.7	149.99	19,674
50	102.5	167.15	24,778
100	103.3	181.95	29,921
150	104.1	194.99	35,103
200	104.9	206.66	40,329
250	105.9	217.23	45,601
300	106.8	226.93	50,921
350	107.9	235.90	56,290
400	109.0	244.28	61,714
450	110.3	252.13	67,194
500	111.7	259.55	72,741
550	113.5	266.61	78,369
600	115.8	273.38	84,101
650	119.0	279.92	89,970
700	123.5	286.29	96,028
726.84 (1000°K)	126.7	289.69	99,379

The equilibrium,

(1) $$UCl_{4(s)} + \tfrac{1}{2}H_{2(g)} \longrightarrow UCl_{3(s)} + HCl_{(g)},$$

has been studied at the UCRL (5, 6) and the results have been critically evaluated by G. MacWood (UCRL 7). The equilibrium constants for this reaction are given in Table 3.

TABLE 3

EQUILIBRIUM CONSTANTS FOR THE REDUCTION OF UCl_4

$$K = \frac{P_{HCl}}{P^{\frac{1}{2}}_{H_2}}$$

Temperature		$\frac{1}{T} \times 10^3$	$K^{(a)}$	$K^{(b)}$
(°C)	(°K)			
400	673	1.486	0.295	0.386
420	693	1.443	0.438	0.549 (425°C)
453	726	1.377	0.789	0.762 (450°C)
477	750	1.333	1.100	1.014 (475°C)
502	775	1.290	1.550	1.277 (500°C)

(a) (UCRL 6).
(b) (UCRL 5).

The change in heat capacity in (1) can be calculated as follows:

$UCl_{3(s)}$: $C_p = 23.42 + 4.132 \times 10^{-3}\ T$

$HCl_{(g)}$: $C_p = 6.7 + 0.84 \times 10^{-3}\ T$

$-UCl_{4(s)}$: $-C_p = -27.56 - 4.412 \times 10^{-3}\ T$

$-\frac{1}{2}H_2\ (g)$: $-\frac{C_p}{2} = -3.31 - 0.408 \times 10^{-3}\ T$

$$\Delta C_p = -0.75 + 1.55 \times 10^{-4}\ T$$

This leads to the expression,

$$\Delta H_T = 17.270 \text{ kcal/mole} - 0.75\,T + 7.79 \times 10^{-5}\,T^2,$$

for the heat of reaction (eq. 1). From the equilibrium constants a value of $\Delta S_{298} = 23.00$ is obtained. Unfortunately this value differs by 3.1 units from that derived from third law considerations ($\Delta S_{298} = 19.92$). The reason for the discrepancy is unknown. If one would assume that the value of the entropy of UCl_4 at 298.16°C derived from the third law, 47.14 e. u. is correct, then the entropy of UCl_3 at 298.16°C would be 40.5 e.u.

Using the latter value, MacWood concludes that the best available data for the reaction,

$$U_{(s)} + 3/2\ Cl_{2\ (g)} \longrightarrow UCl_{3\ (s)}, \tag{7}$$

are:

$$\Delta H_{298} = -212.0 \text{ kcal/mole}; \quad \Delta F^\circ_{298} = -196.7 \text{ kcal/mole}$$

$$\Delta S_{298} = -51.5$$

$$\Delta H = -213,700 + 5.70\,T - 7.79 \times 10^{-4}\,T^2 \tag{8}$$

$$\Delta F^\circ = -213,700 - 13.13\,T \log T + 7.79 \times 10^{-4}\,T^2 + 89.23\,T \tag{9}$$

1.3 Chemical Properties of Uranium Trichloride In this section emphasis will be placed on the reactions of solid UCl_3. UCl_3 is a typical trivalent halide; it resembles the rare earth trihalides in its physical and chemical properties. The principal difference is that UCl_3, both as a solid and in solution, is a strong reducing agent.

(a) Water. Uranium trichloride is hygroscopic, but to a much smaller degree than the other uranium chlorides. No absorption occurs if $p_{H_2O} = 2.4$ mm; slight absorption at $p_{H_2O} = 3.4$. In a nitrogen stream containing water vapor at a $p_{H_2O} = 9$ mm, UCl_3 deliquesces to form a purple solution which slowly evolves hydrogen. In moist air (p_{H_2O} = 9 mm) UCl_3 does not exhibit deliquescence but instead is rapidly hydrolyzed and simultaneously oxidized to $UOCl_2$. The product is a dry cake (Brown 9). UCl_3 gains about 1 per cent by weight per minute on exposure to moist air (UCRL 2).

In water, uranium trichloride dissolves to give a fugitive purple color which soon turns to the dirty green indicative of uranium(IV). Uranium trichloride is soluble in water forming a solution between 3 and 4.8 molar at 0°C. A 0.02 M solution of UCl_3 in water has a pH of about 2.4 (UCRL 8). This is a very rough value but it gives an indication of the extent of hydrolysis.

When UCl_3 is dissolved in water, the amount of hydrogen evolved corresponds within a few per cent to the oxidation from the +3 to +4 state (UCRL 8). The evolution of hydrogen is about one-fourth as rapid at 0°C as at 24°C. At 0°C, UCl_3 can be kept in a saturated solution in contact with the solid salt with little oxidation for considerable periods of time. The oxidation has been followed by the change in absorption spectra. As the oxidation proceeds, the characteristic bands of the U(III) ion (a wide band in the green and two sharp adjacent bands in the red) fade, but the strong band in the yellow-green characteristic of U(IV) does not appear immediately (for explanation, see Chapter 17).

The rate of solution of UCl_3 in hydrochloric acid decreases with increasing concentration: the same weight of crystals which will dissolve completely in 0.5 hours at 0°C in 1 M HCl is not completely dissolved in 1.0 hour in 6 M HCl. Solutions of UCl_3 in concentrated hydrochloric acid are considerably more stable than in water. The heat of solution of UCl_3 in hydrochloric acid (1 mol HCl/8.808 moles H_2O) is 40.6 kcal/mole (Biltz, 1928). It has been reported that the addition of sulfuric acid to an aqueous solution of UCl_3 results in the precipitation of a U(III) sulfate; but the addition of ammonia, phosphoric acid, oxalic acid, or hydrofluoric acid gives only U(IV) salts (Rosenheim, 1908). (See Chap. 12.)

(b) Other Solvents (MP Ames 6, 7; Ephraim, 1933). Uranium trichloride dissolves in glacial acetic acid to a red solution. Methanol or formamide react when treated with UCl_3. Uranium trichloride is insoluble in carbon tetrachloride, acetone, chloroform, pyridine, hydrocarbons or non-polar solvents. In polar solvents the solubility of UCl_3 is less than that of UCl_4 or UBr_4. Uranium trichloride is insoluble in inorganic solvents such as PCl_3 and $SnCl_4$. With PCl_3 a green emulsion is formed.

(c) Thermal Decomposition of UCl_3. When a sample of UCl_3 is heated in vacuum to 840°C, several different substances volatilize and collect in the cooler parts of the apparatus. The material deposited farthest from the furnace is brown UCl_5; nearest the furnace is a light tan deposit of UCl_3, and in-between is a green deposit of UCl_4. Deposition of uranium tetrachloride can first be observed when the temperature reaches 500°C; UCl_5 appears at 720°C and unchanged UCl_3 sublimes first at 840°C. The residue from such sublimation consists of bright, shining, metallic-appearing lumps (UCRL 2). These observations have been interpreted as indicating a disproportionation of UCl_3:

(10) $$2UCl_3 \longrightarrow UCl_2 + UCl_4$$

The evidence for the formation of UCl_2 is, however, far from conclusive (MP Ames 3; MP Chicago 2). (See also Chap. 15)

(d) Oxidizing Agents. When UCl_3 is heated to 700°C in air and then subjected to vacuum distillation, a yellow solid, presumably UO_2Cl_2, sublimes. The probable reaction is (UCRL 2):

(11) $$UCl_3 + O_2 \longrightarrow UO_2Cl_2 + UCl_4$$

Uranium trichloride begins to react with pure oxygen at about 150°C. The product is probably UO_2Cl_2, with some unreacted UCl_3 and a small amount of UO_2 (MP Ames 8). Chlorine reacts with UCl_3 smoothly at 250°C to give UCl_4:

(12) $$UCl_3 + \tfrac{1}{2}Cl_2 \xrightarrow{250^\circ C} UCl_4.$$

Little heat is developed and melting does not occur (MP Ames 2). At higher temperatures, however, the reaction is very vigorous. Thus, when UCl_3 is treated with chlorine at 300°C, the UCl_3 burns, and the reaction mixture reaches an estimated temperature of 800°C. Brown vapors are evolved in this process. When more chlorine is passed over the now solidified reaction mass for six hours at 420°C, a second volatile brown product can be obtained. The first brown sublimate has the composition $UCl_{3.67}$; the second the composition $UCl_{5.33}$. A small amount of green crystals is also obtained; they condense just outside the furnace and have the composition $UCl_{4.83}$. While the analytical results are not particularly good, these observations are reported here because of their bearing on the possible existence of additional uranium-chlorine compounds, similar to U_2F_9 and U_4F_{17} (MP Ames 1). (See Chap. 12.)

Bromine and iodine react with UCl_3 to form mixed halides (MP Ames 9). (See Chap. 15.) Anhydrous hydrogen fluoride oxidizes UCl_3 at elevated temperatures to UF_4 (TEC-CEW 1):

(13) $$UCl_3 + 4HF \xrightarrow{450^\circ C} UF_4 + 3HCl + \tfrac{1}{2}H_2$$

Liquid anhydrous hydrogen fluoride reacts with UCl_3 at 25°C with the evolution of hydrogen chloride; the product is presumed to be UF_3 (Brown 10).

(c) <u>Reducing Agents</u>. Hydrogen has been reported to reduce UCl_3

with the formation of HCl and UCl_2.

(14) $$UCl_3 + \frac{1}{2}H_2 \longrightarrow UCl_2 + HCl$$

However, no experimental details or analytical results are available to substantiate this conclusion (MP Chicago 2). UCl_3 was found to be unattacked by atomic hydrogen at 700°C (MP Chicago 3).

Reduction to uranium metal can be effected by sodium, calcium, lithium and potassium. Of these, calcium and lithium are the best reagents; reduction may be carried out in a beryllia crucible at 1100°C. The reaction should be carried out in a bomb to prevent loss of material by volatilization.

(d) Complex Compounds of UCl_3. A number of complexes containing UCl_3 together with metal halides have been examined by thermal analysis (Brown 8). The results are summarized in Table 4.

TABLE 4

PHASE RELATIONSHIPS OF SOME URANIUM TRICHLORIDE METAL HALIDE SYSTEMS

System	Compounds	M.P. of Compound (°C)	Eutectics	M.P. of Eutectic (°C)
UCl_3-KCl	$2KCl \cdot UCl_3$	625 ± 5	KCl-K_2UCl_5 20 mol % UCl_3	590 ± 5
	$3KCl \cdot UCl_3$	at 530° ± 5 transformed to $2KCl \cdot UCl_3$ and KCl	$2K_2UCl_5$-UCl_3 50 mol % UCl_3	545 ± 5
UCl_3-$NaCl$	None		$NaCl$-UCl_3 33 mol % UCl_3	520 ± 5
UCl_3-$BeCl_2$	None		One undetermined eutectic compd.	635 -640
UCl_3-UCl_4	None		Compounds immiscible in liquid phase and only slightly soluble in the solid phase.	

2. Uranium Tetrachloride

Uranium tetrachloride was first prepared by E. Peligot (1842). Since then the compound has been studied by many workers, particularly at the Radiation Laboratory of the University of California, and at the Tennessee Eastman Laboratories.

A number of halogenation reactions have received study in connection with the preparation of uranium tetrachloride. The heats and free energies of some of them are listed in Table 5. The entropies of halogenation are rather large and this makes it essential to consider free energies rather than heats of reaction in any attempt to predict whether an active chlorinating agent is likely to prove useful.

Table 5 lists free energies at 300°K and 800°K, the latter because temperatures of this order of magnitude are necessary to make most halogenation reactions proceed at a practically useful rate.

Parallelism between the free energy liberated and the rate of establishment of a reaction equilibrium is often observed in a series of analogous reactions but is, of course, not a general rule. Therefore, one cannot be certain that the relative ease with which the various agents listed in Table 5 react with UO_2 corresponds exactly to the order of the ΔF values of halogenation. So much, however, can be predicted: that halogenation reactions which occur without marked decrease in standard free energy will be useless for practical purposes. Even if reactions of this kind, e.g., that with HCl, would proceed rapidly toward equilibrium, the small equilibrium concentration of the reaction products would make it impossible to remove them at a rate allowing conversion to be completed within a reasonable time.

TABLE 5

FREE ENERGIES FOR SOME PREPARATIONS OF URANIUM TETRACHLORIDE

Equation Number	Equation[a]	$\Delta H_{298°K}$[d] (Kcal.)	$\Delta S_{298°K}$[d] (e.u.)	$\Delta F_{300°K}$ (Kcal.)	$\Delta F_{800°K}$ (Kcal.)
(17)	$UO_2 + 4HCl \longrightarrow UCl_4 + 2H_2O$	-8.0	-59.9	+10.0	+39.9
(18)	$UO_2 + C + 2Cl_2 \longrightarrow UCl_4 + CO_2$	-75.1	-28.4	-66.5	-52.3
(19)	$UO_2 + CCl_4 \longrightarrow UCl_4 + CO_2$	-49.4	+5.4	-51.0	-53.7
(20)	$UO_2 + 2CCl_4 \longrightarrow UCl_4 + 2COCl_2$	-36.2	+14.5	-40.6	-47.8
(21)	$UO_2 + 2COCl_2 \longrightarrow UCl_4 + 2CO_2$	-62.5	-3.7	-61.4	-59.5
(22)	$UO_2 + 2SOCl_2 \longrightarrow UCl_4 + 2SO_2$	-37.0	-0.1[c]	-36.7	-36.9
(23)	$UO_2 + \frac{1}{2}S_{2(g)} + 2Cl_2 \longrightarrow UCl_4 + SO_2$[b]	-51.5	-46.1	--	-14.7
(24)	$UO_2 + 2PCl_5 \longrightarrow UCl_4 + 2POCl_3$	-75.4	+8.3[c]	-77.9	--
(25)	$UO_2 + 2PCl_3 + 2Cl_2 \longrightarrow UCl_4 + 2POCl_3$	-117.4	-72.3[c]	--	-59.5

(a) All substances except UCl_4, UO_2 and C are taken in the vapor state.
For UO_2: $S_{298°K}$ = 18.63 e.u.; $\Delta H_{298°K}$ = -270.4 kcal. (see Chap. 11)
For UCl_4: $S_{298°K}$ = 47.14 e.u.; $\Delta H_{298°K}$ = -251.0 kcal. (see Sec. 2.2(e))

(b) This represents the reaction when S_2Cl_2 is used as chlorinating agent.

(c) Entropy of $SOCl_2$ and $POCl_3$ from Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, 1944.

(d) Heats of formation from Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, 1936; entropies from Kelley, "IX. The Entropies of Inorganic Substances," Bur. Mines Bull. 434, 1941.

A point to be kept in mind is that the free energies listed in Table 5 are average values for two chlorination steps, e.g.

(15) $UO_2 + SOCl_2 \longrightarrow UOCl_2 + SO_2$

(16) $UOCl_2 + SOCl_2 \longrightarrow UCl_4 + SO_2$

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In all likelihood the first step liberates more energy than the second one; therefore, if the chlorinating agent is weak, the reaction may stop at the $UOCl_2$ stage.

All the other reagents listed can be expected to convert UO_2 to UCl_4 more or less readily. Carbon tetrachloride and phosgene (reaction 21) appear to be as powerful chlorinating agents, as is thionyl chloride (reaction 22). Phosphorus pentachloride (reaction 24) is especially useful at low temperatures where it does not dissociate into PCl_3 and Cl_2.

Considerations other than thermodynamics, however, enter into the choice of a reagent. It is essential to obtain pure UCl_4, free of the chlorinating reagent; this reduces, for example, the usefulness of sulfur chloride (reaction 23). Corrosion resistance, ease of manipulation and the nature of the other reaction products formed are other factors involved in the selection of a reagent.

The most important starting materials for the preparation of UCl_4 are the uranium oxides. The free metal, hydride, carbide, nitride and sulfide can all be used, but these materials are less readily available. Uranyl compounds, on the other hand, are easily obtainable but insufficiently reactive to be of much value.

An important factor for all chlorination reactions with uranium oxides as material is the "activity" of the oxide used. The existence of oxide preparations of varying activity has been mentioned repeatedly in Chapter 11. It is not quite clear whether activity is a general property of a given preparation or whether it may be somewhat different for various reactions, such as thermal decomposition, reduction with hydrogen or chlorination. Considerable empirical information is available as to the best methods of preparing reactive oxides for halogenation (cf. Chapter 11, p.   ). "Active" uranium dioxide can be obtained, for example, by reduction of the higher oxides with methane, ammonia or ethanol below 750°C; or by thermal decomposition of uranium(IV) compounds such as the sulfate, oxalate or benzoate. Uranium dioxide obtained in this way is a grey-black, pyrophoric powder which oxidizes rapidly in air. The coffee-brown dioxide prepared by reduction or thermal decomposition above 800°C is much more inert. In the case of the trioxide the most reactive form is that prepared by thermal decomposition of uranyl peroxide; UO_3 obtained by ignition of uranyl nitrate or ammonium diuranate is considerably less reactive. Hydrated varieties of the trioxide are quite inert.

The reasons for the variations in reactivity of the oxides are at present not entirely clear, particularly in the case of the dioxide. Recent investigations have shown that uranium trioxide can exist in at least five different crystal forms which differ considerably in thermal stability (see Chapter 11, p.   ). A study of the reactivity of UO_3 and U_3O_8 prepared in different ways for halogenation, undertaken at the Tennessee Eastman Laboratories, unfortunately was carried out apparently without the realization of this extensive polymorphism of the trioxide (TEC-CEW 3). More detailed examination may perhaps reveal a polymorphism also in the case of the dioxide. The reactivity of the oxides may also depend on the exact ratio U:O in the product (according to Chapter 11, p.   ). This ratio can vary in the case of the lower oxide between 1.75 and 2.30 without change in crystal structure.

Halogenation reactions can be carried out either by gas phase reactions in which the vaporized reagent is passed over the uranium compound at elevated temperatures or by liquid phase reactions at more moderate temperatures. Many of the halogenating agents can be utilized in either of these two ways.

Preparative methods for the production of UCl_4 have been critically reviewed by Wagner (TEC-CEW 4); the present discussion follows Wagner's review in many respects.

2.1 Preparation of Uranium Tetrachloride

(a) Uranium Dioxide and Hydrogen Chloride. Thermodynamic data (cf. Table 5) indicate that at elevated temperatures the equilibrium of conversion of uranium dioxide to UCl_4 by hydrogen chloride is not favorable for halogenation. The equilibrium concentrations of UCl_4 and H_2O, calculated from the relationship $-\Delta F = RT \ln K$, are so small that these products cannot be removed rapidly enough to insure a reasonable rate of conversion. It has in fact been found by the Purdue group (Purdue 1) that practically no reaction occurs when UO_2 (prepared by decomposition of uranium(IV) oxalate) is treated with hydrogen chloride in the vapor phase at 400°C. At low temperatures the thermodynamic conditions become less prohibitive. Experiments showed that if a solvent such as water or aqueous alcohol is used, chlorination does occur; however, as anticipated on p. , the oxide is converted only to $UOCl_2$ rather than to UCl_4 (UCRL 9). Uranium trioxide also reacts with hydrogen chloride in ethanol or carbon tetrachloride but, again, only UO_2Cl_2 and no UCl_4 is prodused. Active uranium dioxide has been reported to react with hydrogen chloride in anhydrous ethanol but the formation of UCl_4 in such solutions has not been proved (Purdue 1).

(b) Uranium Oxide, Carbon and Chlorine. Uranium tetrachloride was first prepared by the reaction of chlorine with an intimate mixture of uranium dioxide and carbon (Peligot, 1842); this reaction has since been utilized by many investigators (Zimmermann, 1882; Fischer, 1913; Voight, 1924; Hönigschmid, 1928). Carbon tetrachloride is probably the actual chlorinating agent. In order to obtain an intimate and reactive mixture of oxide and carbon, sugar can be mixed with oxide and ignited. Colani (1907) suggested that sugar charcoal or lampblack is particularly suitable, but other workers have found that carbon obtained in various other ways also is quite satisfactory. Under the conditions of the experiment, involving the passage of a large excess of chlorine, considerable quantities of the uranium pentachloride are also produced (Roscoe, 1874). Biltz and Fendius (1928a) tried to minimize the contamination by the pentachloride by using a large excess of charcoal in the mixture but this device seems to be of little avail. The best ratio of oxide to graphite is about 0.6 (TEC-CEW 5). Any oxide or oxyhalide of uranium can be used instead of the dioxide but, other things being equal, the dioxide will give the least amount of pentachloride. With a sodium uranate-lampblack mixture the reaction proceeds satisfactorily at 600°C (Brown 11).

The principal advantage of this method is readily accessible starting materials. The disadvantages, which seem to outweigh the advantages, are the production of comparatively large amounts of UCl_5 (which must be eliminated by subsequent treatment), the high temperature of reaction which imposes a severe strain on the equipment, and the presence of considerable quantities of phosgene in the waste gases.

Recently this method has again been studied at the Tennessee Eastman Laboratories (TEC-CEW 6). Pellets made by compressing a mixture of uranium trioxide and carbon were supported in a vertical reactor on a perforated graphite disc, chlorine being conducted through the mixture from the bottom. The reaction zone was maintained at 850°C. At this temperature uranium tetrachloride is liquid; it therefore trickles through the bed and collects in the bottom of the reactor. However, large amounts of UCl_5 were formed and swept out as dust in the gas stream. On the whole, the results did not seem too encouraging.

(c) Uranium Oxide and Carbon Tetrachloride Vapor. Carbon tetrachloride was first introduced by Watts and Bell (1878) as an agent for the conversion of metal oxides to chlorides. The utility of this reagent was rediscovered by Demarçay (1887) and Lothar Meyer (1887) who examined its reaction with a large number of oxides. Carbon tetrachloride was first applied to the halogenation of the oxides of uranium by Colani (1907) who found that both U_3O_8 and UO_2 reacted at red heat with gaseous CCl_4. He noticed that the amount of UCl_5 formed concurrently with UCl_4 was much smaller with UO_2 than with U_3O_8. Camboulives (1910), who treated some thirty metal oxides with CCl_4 vapor, also noted that U_3O_8 reacted at 300°C to form a mixture of UCl_4 and UCl_5. These early workers all utilized gaseous carbon tetrachloride at elevated temperatures. Michael and Murphy (1910) were the first to study the halogenation. They used liquid phase liquid CCl_4 as well as solutions of chlorine in CCl_4, and their work forms the basis of the present-day methods of conversion of uranium oxides to UCl_4, UCl_5 and UCl_6 by liquid phase chlorination.

The reaction of various uranium compounds with carbon tetrachloride vapor has been very intensively re-investigated since 1940. All of the

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oxides and a number of other uranium compounds have been shown to form uranium tetrachloride. Thus UO_2 (UCRL 11,12,13; Colani, 1907), U_3O_8 (UCRL 11; Colani, 1907), UO_3 (UCRL 11,12), $UO_4 \cdot 2H_2O$ (UCRL 10), $U(C_2O_4)_2$ (UCRL 12) and $(NH_4)_2U_2O_7$ (UCRL 13) can be converted to UCl_4 of more or less satisfactory purity (cf. Table 6). At sufficiently elevated temperatures uranyl salts, such as the sulfate, chloride and phosphate, can be converted also to UCl_4. In all cases, some uranium pentachloride is formed simultaneously with the tetrachloride. The yield of the latter can be minimized by the use of "active" UO_2 which reacts with CCl_4 at comparatively low temperature and therefore with least oxidation (UCRL 14).

TABLE 6

CONVERSION OF URANIUM COMPOUNDS TO URANIUM TETRACHLORIDE

Starting Material	% U Converted to UCl_4 (a)	% Purity of UCl_4
UO_2 (Commercial)	93	95
UO_3 (Commercial)	87	94
U_3O_8 (Commercial)	83	94
UO_4	70	99
UO_3 (active) (b)	75	97
$(NH_4)_2U_2O_7 \cdot xH_2O$	81	99
$U(C_2O_4)_2$ (c)	91	99
U_3O_8 from $U(C_2O_4)_2$	89	99

(a) The balance of the uranium is considered as being converted to UCl_5.
(b) Prepared from uranyl nitrate.
(c) Partially dehydrated by methanol.

According to the observations made at Berkeley, uranium dioxide suitable for liquid phase chlorination can be obtained by reduction of UO_3 with hydrogen, methane or natural gas at 450°C (UCRL 15). Elsewhere it has been found that particularly active UO_2 can be obtained by reducing UO_3 with ammonia (TEC-CEW 7) or alcohol (Brown 12). The reduction with ethanol is carried out at a temperature of 250°-350°C; the alcohol vapor is introduced mixed with an equal volume of nitrogen. Uranium dioxide so obtained can be halogenated at temperatures as low as 350°-375°C, with comparatively little oxidation to UCl_5.

The course of reaction of uranium dioxide with carbon tetrachloride was studied by measuring and analyzing the gaseous products. At temperatures of 450° ± 20°C (the optimum temperature for the reaction with "inactive UO_2") the principal reaction was found to be (UCRL 16) (cf. equation 19):

$$UO_2 + CCl_4 \longrightarrow UCl_4 + CO_2$$

Small amounts of phosgene, carbon monoxide and chlorine, found in the exit gases (UCRL 14), indicate the occurrence of competitive reactions such as

$$(26) \qquad UO_2 + CCl_4 \longrightarrow UOCl_2 + COCl_2$$

$$(27) \qquad UOCl_2 + CCl_4 \longrightarrow UCl_4 + COCl_2$$

$$(21) \qquad UO_2 + 2COCl_2 \longrightarrow UCl_4 + 2CO_2$$

$$(28) \qquad COCl_2 \longrightarrow CO + Cl_2$$

$$(29) \qquad UCl_4 + \tfrac{1}{2}Cl_2 \longrightarrow UCl_5$$

The principal reaction (19) is exothermic to the extent of about 50 kcal/mole, and local overheating may cause partial fusion and thus lead to incomplete conversion. Attempts have been made to run the reaction at temperatures high enough to sublime the UCl_4 out of the reaction zone; but this procedure appears unsatisfactory since considerable amounts of uranium pentachloride and hexachloroethane are then formed.

The reaction of uranium trioxide with CCl_4 vapor has also received considerable study since direct conversion of UO_3 to UCl_4, without preliminary preparation of UO_2, often appears desirable. The reaction of UO_3 and CCl_4 vapor proceeds under much the same conditions as does that of UO_2 but because of the higher valency of the oxide, the amount of UCl_5 formed is greater. As the temperature is increased from 300° to 350°C the UCl_4 production increases more than that of UCl_5 (UCRL 17), but the proportion of UCl_5 in the product becomes higher (see Table 7).

TABLE 7

FORMATION OF UCl_5 FROM UO_3 AND CCl_4 VAPOR

Temperature (°C)	% Conversion	% UCl_5 formed	% UCl_4 formed	% UCl_5 in UCl_4
300	79.6	8.3	71.3	11.7
350	92.2	11.7	80.5	14.5

With "active" UO_3 from calcined $UO_4 \cdot 2H_2O$ complete chlorination was obtained at 350°C.

The mechanism of this reaction has been studied by methods similar to those employed in the corresponding reaction with UO_2. There appears to be a rapid initial reaction in which carbon dioxide and chlorine are formed and the trioxide is converted to UO_2Cl_2 (UCRL 18).* The second stage of the reaction, the conversion of the oxychloride to tetrachloride, is slow at 400°C. The main stoichiometric reaction at 400°C is considered to be (UCRL 18,19)

(30) $2UO_3 + 3CCl_4 \longrightarrow 2UCl_4 + 3CO_2 + 2Cl_2$.

The following individual reactions have been postulated to account for the presence of $COCl_2$, CO, Cl_2 and UCl_5 among the reaction products:

(31) $UO_3 + CCl_4 \longrightarrow UO_2Cl_2 + COCl_2$

(32) $UO_3 + COCl_2 \longrightarrow UO_2Cl_2 + CO_2$

(33) $2UO_2Cl_2 + 2CCl_4 \longrightarrow 2UCl_6 + 2CO_2$

(34) $2UCl_6 \longrightarrow 2UCl_5 + Cl_2$

(35) $2UCl_5 \longrightarrow 2UCl_4 + Cl_2$

(28) $COCl_2 \longrightarrow CO + Cl_2$

The results obtained with U_3O_8 are intermediate between those found with UO_2 and UO_3. This oxide can be chlorinated at about 450°C with the formation of 8 to 12 per cent UCl_5.

Attempts have been made to control the amount of UCl_5 produced from UO_3 by introducing CO, $CHCl_3$ or other compounds to react with the liberated chlorine

(36) $CO + Cl_2 \longrightarrow COCl_2$

(37) $CH_3Cl_2 + Cl_2 \longrightarrow CCl_4 + HCl$

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* During the course of one experiment the reactor broke accidentally and the content was found to be UO_2Cl_2 and unconverted UO_3.

thereby preventing the formation of UCl_5 (UCRL 20,21). It has been claimed that the presence of CO greatly diminishes the formation of UCl_5 (UCRL 22) but the concensus of opinion is that this expedient is on the whole unsatisfactory. The addition of CH_4, SO_2, $CHCl_3$ and various other chlorinated hydrocarbons was found ineffective. The use of "active" UO_2 and a low temperature of reaction remain the best prescription for the production of UCl_5-free tetrachloride.

Investigations at Tennessee Eastman Laboratories (TEC-CEW 8) indicate that "fluidization" may be a promising method for the preparation of UCl_4 from UO_3. The reaction is carried out in a heated conical reactor through which a vigorous stream of nitrogen is passed, which keeps the uranium oxide particles suspended while they are being halogenated. Because of excellent contact between the UO_3 and the CCl_4, rapid reaction is achieved at a relatively low temperature (350°-450°C), and the proportion of UCl_5 formed is correspondingly minimized.

Numerous types of reactors for both batch and continuous processes have been devised for the vapor phase halogenation of the uranium oxides with CCl_4. For their description, we refer to the previously mentioned survey of Wagner (CEW-TEC 4).

(d) Liquid Phase Reaction of UO_3 and CCl_4; Decomposition of UCl_5. It was found by the Brown University group that UO_2 or UO_3 react slowly with liquid CCl_4 at the boiling point (77°C) to give UCl_4 (Brown 2). Higher temperatures and pressures greatly accelerate the liquid phase reaction. Thus, uranium dioxide rapidly reacts with liquid CCl_4 at 250°C.

The higher uranium oxides react more easily, i.e., at lower temperatures and pressures, than does UO_2; consequently, the greatest attention has been paid to the reaction of liquid CCl_4 with UO_3. The conditions under which this reaction occurs depend to a very considerable extent on the nature of the uranium trioxide. The most reactive material is the trioxide obtained by thermal decomposition of $UO_4 \cdot 2H_2O$ at 350°C (Brown 13). Other compounds such as U_3O_8 (UCRL 23), UO_2Cl_2, $UO_2(NO_3)_2$ and UO_2F_2 undergo similar reactions but the product is not always pure UCl_4.

At 115°-185°C the primary reaction product of UO_3 and liquid CCl_4 probably is UCl_5:

$$2UO_3 + 6CCl_4 \rightleftharpoons 2UCl_5 + 6COCl_2 + Cl_2 \qquad (38)$$

If phosgene and chlorine are removed from the reactor or if the reaction is carried out at too high a temperature, the UCl_5 decomposes to UCl_4 and Cl_2. Thus, by changing the conditions, the reaction may be made to yield either UCl_5 or UCl_4. To obtain UCl_4 as pure as possible, the reaction is carried out at 120°C; the temperature is then gradually raised to 160°C, while venting the phosgene and chlorine. After several hours at 160°C, UCl_4 is found to be the sole remaining reaction product. Since UCl_4 produced in this way usually is either a fine powder or consists of hard lumps which are difficult to remove quantitatively from the reactor, it may be more convenient to use a two-step process: Uranium pentachloride is prepared first (in the way described in Section 3.1) and then decomposed in a separate step.

Uranium pentachloride undergoes decomposition to the tetrachloride when heated in a stream of nitrogen, carbon dioxide or even chlorine (Brown 3,4,6,14,15,16,17; MP Ames 10):

(35) $2UCl_5 \rightleftharpoons 2UCl_4 + Cl_2$

Decomposition begins below 100°C and is complete at 250°C. The volatility and poor heat conductivity of the UCl_5 cause some complications in the practical de-chlorination procedure. The de-chlorination can be smoothly effected by placing the UCl_5 in a narrow, vertical glass cylinder which is then slowly lowered into a furnace maintained at 500°C. A stream of carbon dioxide or nitrogen is played on the surface of the UCl_5 to help to condense the material which may otherwise be lost by sublimation.

De-chlorination of UCl_5 can also be accomplished by refluxing with S_2Cl_2, $SnCl_4$, C_3Cl_6, etc. (TEC-CEW 9). It is usually difficult, however, to free the product from the solvent. Thionyl chloride works better; with this reagent, both de-chlorination and removal of the solvent can be achieved without much difficulty (TEC-CEW 10).

(e) <u>Chlorination in the Vapor Phase with Other Organic Halogen Compounds</u>. A large number of halogenated organic compounds have been examined as reagents which might convert uranium oxides to UCl_4 at low temperatures without formation of phosgene or UCl_5. These compounds are listed in Table 8. In general, compounds with more than four carbon atoms are unsatisfactory because of excessive carbon formation. Chloroform and $CHCl_3$-CCl_4 mixtures also produce considerable carbonization. Chloroform itself reacts slowly; conversion is incomplete and the UCl_4 is contaminated with pyrolytic products (UCRL 21). Hexachloropropene and hexachlorocyclopentadiene - unsaturated compounds which have chlorine atoms in the alpha position relative to a double-bonded carbon atom - are fairly satisfactory. However, none of these compounds has any advantages over carbon tetrachloride as far as vapor phase chlorination is concerned.

TABLE 8*

ORGANIC COMPOUNDS WHICH HAVE BEEN TESTED AS HALOGENATING AGENTS FOR URANIUM TRIOXIDE

Compound	Formula
Methyl Chloride	CH_3Cl
Methylene Chloride	CH_2Cl_2
Chloroform	$CHCl_3$
Carbon Tetrachloride	CCl_4
1,1,1 Trichlorethane	CH_3CCl_3
s-Tetrachlorethane	$CHCl_2CHCl_2$
Hexachlorethane	CCl_3CCl_3
1,2,3 Trichlorpropane	$CH_2ClCHClCH_2Cl$
Trichlorethylene	$CCl_2{=}CHCl$
Tetrachlorethylene	$CCl_2{=}CCl_2$
Trichloracrylyl chloride	$Cl_2C{=}CCl{-}COCl$
Hexachlorbutadiene	$CCl_2{=}CCl{-}CCl{=}CCl_2$
Trichlorcumene	$(CH_3)_2CHC_6H_2Cl_3$
Chloral	CCl_3CHO
Trichloracetyl chloride	CCl_3COCl
Allyl chloride	$CH_2{=}CHCH_2Cl$
2,3 Dichloropropylene - 1	$H_2C{=}CCl{-}CH_2Cl$
Hexachloropropene	$CCl_2{=}CClCCl_3$
Hexachlorocyclopentadiene	C_5Cl_6
Benzotrichloride	$C_6H_5CCl_3$

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* (UCRL 24; TEC-CEW 11,33; Purdue 2)

(f) Liquid Phase Chlorination with Hexachloropropene. While chlorinated organic compounds other than CCl_4 offer little advantage in vapor phase reactions, the situation is markedly different in the case of liquid phase halogenations. It has been found at the Tennessee Eastman Laboratories that liquid hexachloropropene is an excellent reagent for producing UCl_4 (TEC-CEW 12,33). Some physical properties of hexachloropene are summarized in Table 9.

TABLE 9 *

SOME PHYSICAL PROPERTIES OF HEXACHLOROPROPENE

Physical Property	Value
Boiling Point	210°C (760 mm) 98°C (11 mm)
Melting Point	-70°C
N_D^{20}	1.551
Dispersion	0.0152
Density	1.714 g/cc (25°C)
Dielectric Constant	2.72

* (Purdue 3)

Refluxing for a short time with hexachloropropene converts UO_3, U_3O_8, $UO_2 + 2UO_3$, $UO_4 \cdot 2H_2O$, UO_2Cl_2, UO_2SO_4, $UO_2(NO_3)_2$ and other uranyl compounds to UCl_4. Pure uranium dioxide and $(NH_4)_2U_2O_7$ do not undergo this reaction (Purdue 4; TEC-CEW 9,13,33). It has further been found at Tennessee Eastman that $MoCl_4$, WCl_6, $WOCl_4$, $CoCl_3$, $CbCl_5$, $TaCl_5$, VCl_3 and

$HgCl_2$ also can be easily prepared by refluxing the corresponding oxide with hexachloropropene (TEC-CEW 14).

With UO_3, a rapid and exothermic reaction starts below 100°C. Uranium pentachloride, which is easily soluble in the reaction mixture, forms first and it is then decomposed by further heating to 165°C. Reaction is incomplete if the molal ratio of hexachloropropene to uranium trioxide falls below 5:1; the UCl_4 should be washed with CCl_4 (after filtration) to remove the last traces of organic matter.

The principal organic product of the reaction is trichloroacrylyl chloride, $CCl_2=CClCOCl$ (b.p. 159°C) (Purdue 5, TEC-CEW 13,33). Since this compound tends to hold uranium in solution, it should be removed by distillation before attempting the isolation of the UCl_4.

Chlorination of UO_3 with hexachloropropene in the liquid phase has been carried out also in autoclaves (TEC-CEW 15). "Average" UO_3 begins to react at 90°C and develops about 50 psi pressure; the drier the oxide, the lower the pressure developed in the system.

A large number of organic halogen compounds have been examined for utility in liquid phase halogenation (TEC-CEW 11,33) (see Table 8). The saturated chlorine compounds must have a much higher boiling point than CCl_4 in order to show appreciable reaction and are, on the whole, not very effective. Compounds with a vinylic chlorine (i.e., a C=C-Cl group) have little chlorinating capacity, as may be expected from the general inertness of such chlorine atoms in substitution reactions. Trichloroacrylyl chloride, however, reacts with UO_3 to form a water-insoluble compound, which is soluble in acetone or benzene and appears to be a partially chlorinated oxide. Compounds with an allylic chlorine (a C=C-CCl group) are in general much more effective; hexachloropropene (discussed above) is the best known reagent in this class. Hexachlorocyclopentadiene, C_5Cl_6, and benzotrichloride, $C_6H_5CCl_3$, react vigorously but it has not been possible as yet to isolate pure UCl_4 from the reaction mixtures.

A number of chlorinated hydrocarbons have been studied as halogenating agents for UO_3, using sealed glass bomb tubes (TEC-CEW 16). CBr_2Cl_2 and $CBrCl_3$ produce pure UCl_4. At 130°C, $CH_3COCCl_2COCH_3$, CCl_3CHO, CCl_3COCl, CH_3CHCl_2, $CCl_2{=}CCl_2$, $CH_2ClCHCl_2$, $CCl_3COOCH_2CH_3$, $CHCl{=}CCl_2$, CCl_3CN, CH_3CCl_3, and $CH_3CCl_2CH_3$ are less satisfactory. These compounds are arranged in order of decreasing reactivity. Chloroform does not react even in the presence of appreciable quantities of UCl_5.

(g) <u>Uranium Oxide and Phosgene</u>. Phosgene was introduced as a halogenating agent by Chauvenet (1911), who found it to be a powerful reagent of wide applicability. Reaction occurs not only with uranium oxides but also with sulfides and phosphates. Thus, the mineral, autunite, reacts at 800°C:

$$(39) \qquad 2UO_2 \cdot CaO \cdot P_2O_5 + 8COCl_2 \longrightarrow 2UCl_4 + 2POCl_3 + 8CO_2 + CaCl_2$$

Chauvenet found the reaction of phosgene with U_3O_8 to proceed at 450°C; this was confirmed by Rosenheim and Kelmy (1932). "Active" UO_2 reacts at slightly lower temperatures. In recent work, phosgene has not been utilized extensively, presumably because of its poisonous properties. British workers have observed complete conversion of U_3O_8 to UCl_4 by $COCl_2$ at 900°-940°C (British 1). Phosgene has been used on a commercial scale for the conversion of thorium dioxide to anhydrous chloride, and there is little doubt of its general efficacy in the preparation of anhydrous chlorides.

(h) Uranium Oxide and Thionyl Chloride (UCRL 24; Purdue 1,2,4,6). Thionyl chloride is an effective reagent for converting the uranium oxides to UCl_4. In the vapor phase, UO_3 (obtained by decomposition of the peroxide) is rapidly converted to UCl_4 at 350°C. U_3O_8 reacts less rapidly. Both $UO_4 \cdot 2H_2O$ and $(NH_4)_2U_2O_7$ can be chlorinated at 350°C. The most satisfactory oxide from the point of view of the least UCl_5-contamination is "active" UO_2 (prepared from $UO_4 \cdot 2H_2O$ or UO_3 by reduction with alcohol vapor) (UCRL 5).

In the liquid phase "active" UO_3 can be converted to UCl_5 by refluxing with $SOCl_2$. The addition of UCl_5 aids the reaction. Difficulties are encountered in isolating UCl_5 from the reaction mixture because of the high solubility of UCl_5 in $SOCl_2$ (Table 10).

TABLE 10 *

SOLUBILITY OF SOME URANIUM COMPOUNDS IN LIQUID THIONYL CHLORIDE

Compound	Solubility ($g/ml\ SOCl_2$)
UCl_4	3×10^{-4}
UCl_5	1.29
UCl_6	0.17
UO_2Cl_2	3×10^{-4}

* (TEC-CEW 17)

A reddish compound, $UCl_5 \cdot xSOCl_2$, crystallizes from such solutions; this complex may be decomposed at 100°C in vacuum. Solutions of UCl_5 in $SOCl_2$ can be simultaneously de-chlorinated and de-solvated also by spray-drying at 300°C (TEC-CEW 10).

Chlorination of UO_3 with liquid $SOCl_2$ has been carried out at 100°-130°C and 75-150 psi (Purdue 4; TEC-CEW 8). The reaction may be directed so as to produce either UCl_4 or UCl_5 but the results are rather unpredictable.

Sulfuryl chloride, SO_2Cl_2, does not chlorinate either UO_3 or U_3O_8.

(i) Uranium Oxide and Sulfur Chloride. Sulfur monochloride, S_2Cl_2, was first suggested as a chlorinating agent by Matignon and Bourion (1905) and the reaction was later applied to uranium oxides by a number of workers. Colani (1907) found that a mixture of chlorine and S_2Cl_2 reacts with U_3O_8 at red heat but that unless the UCl_4 is sublimed away, the reaction is incomplete. Considerable amounts of UCl_5 are formed. Lely and Hamburger (1914) found that if S_2Cl_2 was used without chlorine, conversion to UCl_4 occurred without much UCl_5 formation (see also Hulzmann, 1934). R. W. Moore (1923) has given a detailed description of the preparation of UCl_4 by reaction of S_2Cl_2 with U_3O_8. Goggin (1926) studied the reaction of U_3O_8 with S_2Cl_2 and chlorine at 900°C, conducted in such a way that reaction and sublimation could proceed simultaneously.

"Active" oxides begin to react at 250°C and reaction is usually complete below 450°C. At elevated temperatures the reagent is actually dissociated into sulfur and chlorine.

Thermodynamically, the process,

$$(40) \qquad UO_2 + 2S_2Cl_2 \longrightarrow UCl_4 + SO_2 + 3S,$$

is more favorable than

$$(41) \qquad 2UO_2 + S_2Cl_2 + 3Cl_2 \longrightarrow 2UCl_4 + 2SO_2.$$

The use of chlorine as a carrier gas is advisable, however, since contamination of the product by sulfur should be reduced by its use. The reaction proceeds at much lower temperatures in the liquid phase. A 95 per cent conversion can be effected by refluxing U_3O_8 with S_2Cl_2 (138°C) for seven hours at atmospheric pressure (Brown 2,14; UCRL 24). All of the oxides of uranium undergo this reaction. Higher pressures facilitate the conversion. The product is usually heavily contaminated with sulfur, which is difficult to remove. It is practically impossible to remove it by vacuum sublimation (British 1,2; Nat. Bur. Standards 2). It has been proposed to purify sulfur-containing UCl_4 by treatment with chlorine, which was expected to convert sulfur into volatile SCl_4 (UCRL 26), but large amounts of UCl_5 may be formed under these conditions.

(j) Chlorination with Other Anhydrous Inorganic Chlorides (TEC-CEW 19,20; UCRL 26). The chlorination of UO_2 by a large number of inorganic halides has been studied, particularly at the Tennessee Eastman Laboratories. Thermodynamically, reaction can be expected only with the halides of metals which form very stable oxides, since UO_2 itself is very stable. None of the reagents studied proved to be particularly useful, except perhaps aluminum trichloride. Ammonium chloride, which is widely used for the conversion of rare earth oxides to chlorides, fails in the case of uranium (Booth, 1939). The results of UO_2-metal halide reactions are summarized in Table 11.

TABLE 11

REACTION OF UO_2(a) WITH INORGANIC HALIDES

Halide	Conditions(b)	Result
NH_4Cl, CuCl, KCl, Hg_2Cl_2	Fusion at melting point of salt	No reaction
$CaCl_2$	700° - 800°C	5% UCl_4
$BeCl_2$	500°C	Complete conversion to UCl_4 in 4 hours
$MgCl_2$	700° - 800°C	15% UCl_4
$SnCl_2$, $ZnCl_2$	500°C	Small amount of green sublimate
$NiCl_2$, $CuCl_2$, $FeCl_2$, $CoCl_2$, $CdCl_2$, $PbCl_2$, $HgCl_2$, $BaCl_2$, $MnCl_2$	500°C	No reaction
$AlCl_3$	250°C	Reacts readily
$SbCl_3$	Reflux	No chlorination
PCl_3	Reflux	5% UCl_4
$FeCl_3$	300°C	An unidentified U compound (not UCl_4)
$SiCl_4$	Reflux	No reaction
$SnCl_4$	Reflux	No reaction
PCl_5	300°C	20% conversion
$TaCl_5$	Reflux	10-20% UCl_4

(a) Mallinckrodt UO_2, which is very unreactive, was used in these experiments.

(b) Where the temperature is above the boiling point of the halide, the reaction was run in a bomb tube.

Uranium tetrafluoride has also been studied in respect to its behavior toward many of the above-mentioned reagents. It can be readily converted to UCl_4 with $AlCl_3$ and BCl_3 in the vapor phase (TEC-CEW 21). In the liquid phase UF_4 can be converted to UCl_4 to the extent of 5 per cent by refluxing with $SiCl_4$ (1 hour), to the extent of 10 to 20 per cent by refluxing with $SbCl_3$ (2 hours); 80 per cent conversion can be achieved by refluxing with $SnCl_4$ (2 hours) and a 90 per cent yield by refluxing with $TaCl_5$ (1 hour). As could be anticipated from the heats of formation of the fluorides, fusion of UF_4 with NaCl, KCl, CuCl, $NiCl_2$, $MnCl_2$, $PbCl_2$ and $SnCl_2$ yields no UCl_4; but $BeCl_2$, $MgCl_2$, $CaCl_2$, $BaCl_2$ and $NaAlCl_4$ convert UF_4 to UCl_4 at 700°-800°C (TEC-CEW 22). It is difficult to recover UCl_4 free from the chlorinating agent from the products of these reactions.

Uranium(IV) sulfate and the eutectic mixture $NaCl+CaCl_2$ (51.5 per cent $CaCl_2$) yield a sublimate of UCl_4 when heated to 750°C in vacuum; 10 per cent conversion can be obtained after several hours. With $BaCl_2$ at 580°C, only a small amount of green sublimate is obtained after thirteen hours (Purdue 1).

(k) Preparation of UCl_4 in Aqueous Solution. Aqueous solutions of UCl_4 can be readily prepared by reduction of uranyl chloride solutions. Reduction may be effected electrolytically, photochemically, by amalgams of silver, cadmium, or bismuth, by metallic copper, or by sodium hyposulfite, $Na_2S_2O_4$ (Zimmermann, 1882; Kohlschütter, 1900; Giolitti, 1905; Aloy, 1922). Treatment with air may be required to oxidize any U(III) which is formed.

Attempts to isolate anhydrous UCl_4 from such solutions have been only partially successful. Rosenheim and Kelmy (1932) reported the preparation of the hydrate $UCl_4 \cdot 10H_2O$ by evaporation of the aqueous solution to a syrup, followed by treatment with absolute alcohol saturated with hydrogen chloride. The Ames group was unable to confirm this result. The product they obtained by dehydration in a stream of hydrogen chloride was a mixture of UO_2 and $UOCl_2$ (MP Ames 11). This result later was also confirmed by other investigators.

The direct dehydration of U(IV) solutions according to the procedure of Kleinheksel and Kremers (1928), which is very effective for rare earths, does not give anhydrous UCl_4. However, the $UOCl_2$ which can be obtained in this way may be converted, at least in part, to UCl_4 by thermal disproportionation (UCRL 9) (see Chapter 16).

Promising results have been obtained by dehydration of aqueous UCl_4 solutions by azeotropic distillation (TEC-CEW 23). Benzene, carbon tetrachloride, chloroform, etc. have been added to the aqueous solution of UCl_4 and the azeotrope distilled until all of the water has been removed. Removal of the dehydrating solvent itself leaves solid, green products from which 10-70 per cent of UCl_4 can then be obtained by sublimation.

(1) *Miscellaneous Preparations of UCl_4. Halogenation of Various Uranium Compounds.* Uranium metal readily reacts with many halogenation agents to give the tetrachloride (Péligot, 1842; Zimmermann, 1882; Moissan, 1896):

$$U + 2Cl_2 \xrightarrow{250^\circ C} UCl_4 \qquad (43)$$

Hydride can be used instead of the metal (see Chapter 8):

$$(44) \qquad UH_3 + 2COCl_2 \xrightarrow{250^\circ C} UCl_4 + 2CO + 3/2\ H_2$$

$$(45) \qquad UH_3 + 7/2\ Cl_2 \longrightarrow UCl_4 + 3HCl$$

At higher temperatures uranium metal also reacts with CH_3Cl or HCl. The direct reaction of UH_3 with chlorine is not suitable for laboratory use since, once it has started at 200°C, it cannot be controlled. The reaction sequence:

$$(46) \qquad U + 3/2\ H_2 \longrightarrow UH_3$$

$$(2) \qquad UH_3 + 3HCl \longrightarrow UCl_3 + 3H_2$$

$$(12) \qquad UCl_3 + 1/2\ Cl_2 \longrightarrow UCl_4$$

is much more convenient when uranium metal is to be converted to UCl_4 (MP Ames 2).

Uranium sulfide (UCRL 26) and carbide (Moissan, 1897) can be chlorinated with chlorine gas at 400°C; the carbide also reacts with hydrogen chloride at elevated temperatures. Uranium nitrides, UN and $UN_{1.75}$, react readily with hydrogen chloride at 400°-500°C to yield a mixture of ammonium and uranium chlorides (MP Ames 12). (See Chapter 10.) Most uranyl salts are susceptible to chlorination in the vapor phase, but react more slowly than the oxides. Uranates and diuranates are partially chlorinated in the liquid phase by carbon tetrachloride but the products have not yet been well characterized (TEC-CEW 22).

Attempts have been made to convert organic U(IV) compounds to UCl_4

by double decomposition. Thus, uranium(IV) acetyl acetonate has been treated, in benzene or ethyl ether solution, with anhydrous hydrogen chloride. Black tars resulted and no UCl_4 could be isolated (UCRL 27). As is also the case with thorium, the white solid which first precipitates when the solution is treated with hydrogen chloride still contains organic matter. Uranium(IV) benzoate, $U(OOCC_6H_5)_4 \cdot H_2O$, suspended in ethyl ether and treated with anhydrous hydrogen chloride yields green compounds with chlorine:uranium ratios between 2.5 and 3.8, which contain 20 to 40 per cent organic matter (TEC-CEW 24). The green product dissolves in water to a green solution, but no UCl_4 can be obtained from it by sublimation.

(m) Purification of Uranium Tetrachloride. Uranium tetrachloride can be purified either by direct sublimation in vacuum or by sublimation as a higher chloride in a stream of chlorine (275°-700°C) and subsequent reconversion to UCl_4 (Brown 14). Sublimation can also be performed in a stream of inert gas such as nitrogen or helium. In nitrogen, sublimation is rapid at 600°-650°C at a pressure of 3 to 5 mm; the UCl_4 sublimes without melting. If the sublimation is performed at atmospheric pressure, the non-volatile residue can be greatly reduced by adding CCl_4 to the nitrogen stream (Brown 3). Helium with a small admixture of chlorine has been used for the same purpose.

A suitable purification procedure, especially when considerable quantities of material are involved, is vacuum sublimation (UCRL 28,29,30). The stainless steel still operates at 700°C and a pressure of 5×10^{-5} mm Hg.

Tennessee Eastman Laboratory investigators highly recommend fractional condensation in vacuum as a purification method. The condenser possesses a thermal gradient, and the UCl_4 collects in the region held at 325°-410°C (TEC-CEW 25,34).

The quality of purified UCl_4 can be evaluated by several criteria, the most important ones being solubility in certain selected solvents and volatility (Purdue 7,8; TEC-CEW 26).

2.2 Physical Properties of UCl_4

(a) Melting Point. The most reliable value of the melting point of UCl_4 determined is 590° ± 1°C (TEC-CEW 27,35). The unweighted average of a number of determinations made by various other observers is 589°C (MP Ames 13; Brown 3,5,8; UCRL 32,33,34). The published value of 564°C (Voight, 1924) is definitely too low.

(b) Transition Points. A study of the cooling curve of UCl_4 showed solid-solid transitions at 212°C, 506°-522°C and 543°-565°C. Only small heat effects (~1 kcal/mole) appeared to be associated with these transitions (UCRL 31). Observers at the National Bureau of Standards (NBS 3) were unable to confirm the phase transition at 211°C. The reality of all the phase transitions therefore remains uncertain.

(c) Boiling Point. The best direct measurement of the boiling point of UCl_4 (made at the Tennessee Eastman Laboratories) gave 792°C at 760 mm Hg pressure (TEC-CEW 27,35). There appears to be no appreciable decomposition at this temperature. Several other determinations of the boiling point are of doubtful accuracy (MP Ames 14,15; UCRL 32).

(d) Vapor Pressure. The vapor pressure of solid UCl_4 has been determined by two methods - by effusion at Berkeley and by transpiration at Ames. The results disagree. The reason for this is not obvious, but the effusion data probably are more reliable. According to a critical survey of the effusion measurements (UCRL 35), the vapor pressure of the solid UCl_4 can be expressed by the equation

$$\text{(47)} \qquad \log p_{mm} = -\frac{10427}{T} + 13.2995 \qquad (350^\circ - 505^\circ C).$$

Values calculated from this equation are given in Table 12. The heat of sublimation is 47.7 kcal/mole, and the free energy of sublimation is given by the equation:

$$\text{(48)} \qquad \Delta F^\circ = 60606 + 36.85\,T \log T - 170.9\,T \qquad \text{(cal/mole)}$$

TABLE 12

VAPOR PRESSURE OF SOLID URANIUM TETRACHLORIDE

Temp. (°C)	Pressure (mm Hg)	Temp. (°C)	Pressure (mm Hg)
350	0.00037	430	0.030
360	0.00067	440	0.047
370	0.0012	450	0.076
380	0.0022	460	0.12
390	0.0038	470	0.18
400	0.0064	480	0.28
410	0.011	490	0.43
420	0.018	500	0.64
		505	0.80

The vapor pressure of <u>liquid</u> UCl_4 has been determined at the Tennessee Eastman Laboratories (TEC-CEW 27,35); the results obtained there supersede the older values (UCRL 32). The results can be expressed by the equation:

$$\log p_{mm} = -\frac{7205}{T} + 9.65 \qquad (590^\circ\text{-}790^\circ C) \tag{49}$$

Experimental values are given in Table 13 and plotted in Fig. 1. The heat of vaporization calculated from these data is 33 kcal/mole. The latent heat of fusion is then 47.7 - 33 = 14.7 kcal/mole, and Trouton's constant is 31. Liquid UCl_4 thus appears to be a highly associated liquid.

TABLE 13

VAPOR PRESSURE OF LIQUID URANIUM TETRACHLORIDE

Temp. (°C)	Pressure (cm Hg)	Temp. (°C)	Pressure (cm Hg)
789.5	74.63	714	23.0
788	74.55	697.5	17.2
791	74.26	692	15.0
769	54.6	660	9.0
770	54.1	648	6.1
763.5	54.0	639	6.0
761	47.2	632	4.7
757	46.0	628	4.6
747	39.5	611	3.2
742	37.4	603	2.7
733	30.9	597	2.3
727.5	28.0	591	1.9

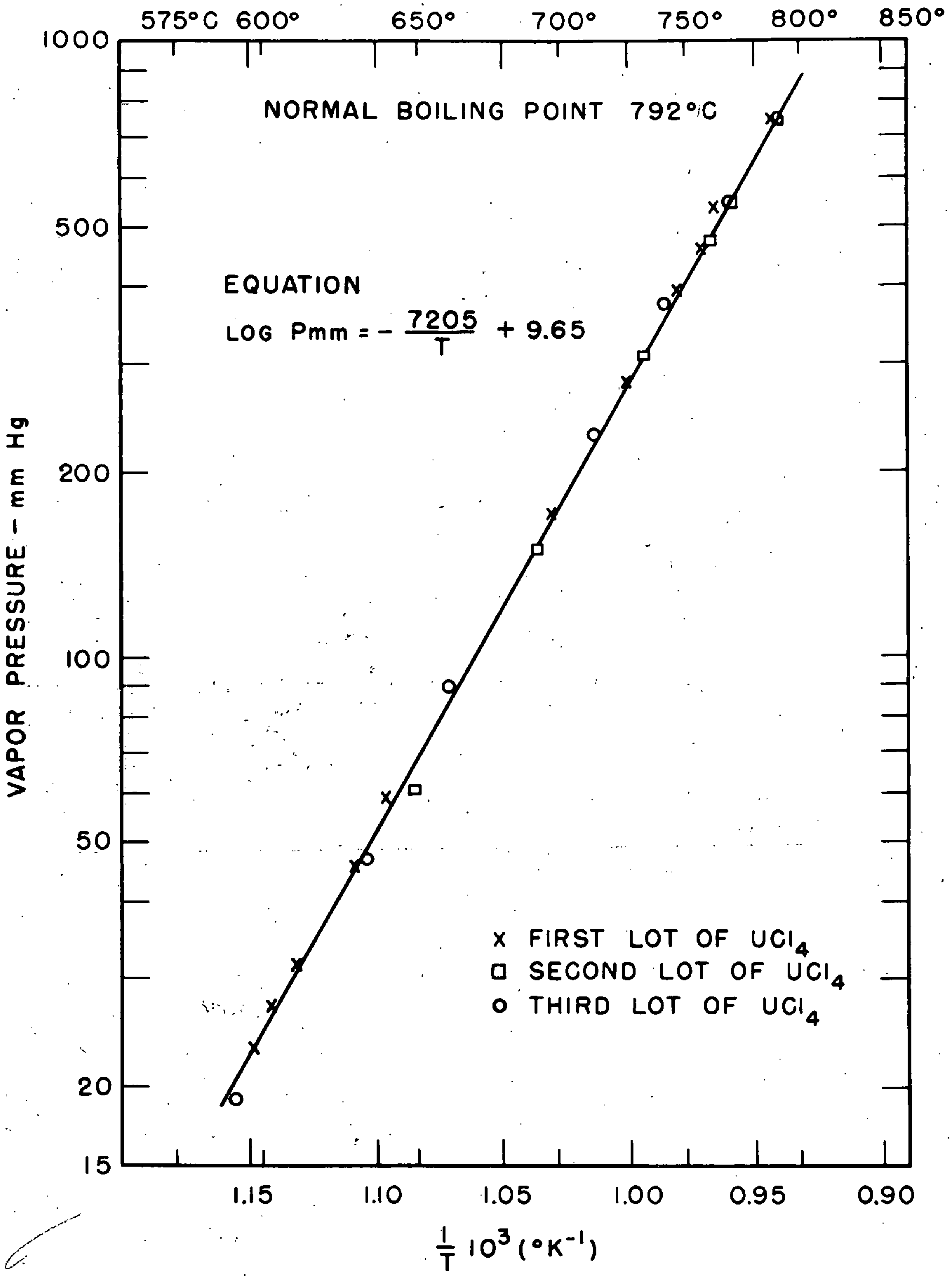

FIG. I. VAPOR PRESSURE OF LIQUID URANIUM TETRACHLORIDE.

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Extrapolation of the vapor pressure curves of liquid UCl_4 gives $p = 19.5 \pm 1$ mm for the vapor pressure at the melting point, 590° ± 1°C. This gives the best available estimate for the triple point coordinates.

The vapor pressure measurements made at Ames by the transpiration method (MP Ames 15) gave results of an altogether different order of magnitude (much higher than those listed in Table 13). They must contain a systematic error and will not be further discussed here.

(e) Crystal Structure and Density. Uranium tetrachloride forms metallic, dark-green octahedral crystals. X-ray study (MP Chicago 4,5) shows that they have tetragonal symmetry, with the lattice constants

$$a_1 = 8.296 \pm 0.009\text{A} \qquad a_3 = 7.487 \pm 0.009\text{A}$$

There are four UCl_4-molecules per unit cell, and the calculated density is 4.87 g/cc. The symmetry group is I4/amd, and the position of the atom is as follows:

4 U in 4 (b)

16 Cl in 16 (h) with $x = 0.281$, $z = 0.398$

These Chicago results have later been confirmed elsewhere (Johns Hopkins 1,2; MP Ames 16).

The density has been determined also by direct measurement. The older values were 4.854 (Biltz, 1928a) and 4.725 (Hönigschmid, 1928). The density has been determined by gas displacement with hydrogen from room temperature down to liquid air temperatures (Hülsmann and Biltz, 1934). These workers obtained 4.950 at -193°C and 4.890 at -78°C. Their value at 19°C agrees well with the x-ray density. The Ames group finds a density of 4.88 g/cc at 24°C which also checks the x-ray value very well (MP Ames 10).

The density of UCl_4 vapor also has been measured (Zimmermann, 1881). The average value is 13.31 (referred to air); it shows that no association takes place. An ebullioscopic determination of the molecular weight in bismuth trichloride as solvent indicates that UCl_4 is present in the form of simple molecules in solutions also - at least, in dilute solutions at high temperatures (Rugheimer, 1908).

(f) Thermochemical Data. Observers of the National Bureau of Standards (4) have determined the specific heat*, entropy and enthalpy of $UCl_{4(s)}$ from 15° to 355°K (Table 14). Measurements were made in an atmosphere of dry helium to avoid oxidation and hydrolysis. The values of S and the function $H-E_0^0$ were obtained by tabular integration, using Simpson's rule. The entropy of $UCl_{4(s)}$ at 298.16°K is 47.14 e.u. These results have been extended in a second series of determinations (National Bureau of Standards 3), which also covered the temperature range 0°C to 427°C (Table 15). The differences between the two sets of values in the range where overlapping occurs is about 0.4 per cent; the high temperature values (Table 15) are probably more reliable since the UCl_4 used was of better quality.

The following equations fit the experimental data in Table 15 with the indicated precision. They should not be used for temperatures below 0°C.

$$(50) \qquad C_p = 0.07608 + 2.88 \times 10^{-5}\, t - \frac{1.3}{(t+41)^2} \qquad \text{(cal/g °C)}$$

$$(\pm\, 0.35\%,\ 0\text{–}427°\text{C}) \qquad \text{(t in °C)}$$

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* The sample used contained less than 0.02 per cent of non-volatile impurities.

TABLE 14

SPECIFIC HEAT, ENTROPY AND ENTHALPY OF URANIUM TETRACHLORIDE FROM 0°K TO 355°K

T°K	C_p Int. joules/(mole °K)	S Int. joules/(mole °K)	$H-E_0^s$ Int. joules/(mole °K)
0	0.0	0.0	0.0
5	0.255 (a)	0.0843	0.318
10	2.035 (a)	0.6793	5.098
15	6.473	2.251	25.22
20	13.01	4.977	73.55
25	20.50	8.673	156.9
30	28.17	13.09	278.8
35	35.27	17.98	437.6
40	41.64	23.11	630.2
45	47.26	28.35	852.5
50	52.24	33.59	1102.0
55	56.68	38.79	1374.
60	60.78	43.88	1668.
65	64.73	48.93	1982.
70	68.34	53.83	2314.
75	71.72	58.66	2665.
80	74.88	63.40	3032.
85	77.80	68.04	3413.
90	80.61	72.56	3809.
95	83.12	76.97	4219.
100	85.48	81.30	4640.
105	87.72	85.55	5074.
110	89.85	89.66	5517.
115	91.82	93.72	5972.
120	93.72	97.63	6435.
125	95.47	101.5	6908.
130	97.10	105.3	7390.
135	98.66	109.0	7879.
140	100.1	112.6	8376.
145	101.5	116.1	8880.
150	102.8	119.6	9391.
155	103.9	123.0	9908.
160	105.0	126.3	10430.
165	106.1	129.5	10959.
170	107.1	132.7	11491.
175	108.0	135.9	12029.
180	108.9	138.9	12571.
185	109.7	141.9	13118.
190	110.5	144.9	13668.
195	111.2	147.7	14223.

TABLE 14 (CONT'D)

T°K	C_p Int. joules/(mole °K)	S Int. joules/(mole °K)	$H-E_0^s$ Int. joules/(mole °K)
200	111.9	150.6	14781.
205	112.6	153.3	15342.
210	113.2	156.0	15906.
215	113.8	158.7	16474.
220	114.4	161.3	17045.
225	115.0	163.9	17618.
230	115.5	166.4	18194.
235	116.1	168.9	18773.
240	116.6	171.4	19355.
245	117.0	173.8	19939.
250	117.5	176.2	20525.
255	118.0	178.5	21114.
260	118.5	180.8	21705.
265	118.9	183.0	22298.
270	119.4	185.3	22894.
275	119.8	187.5	23492.
280	120.3	189.6	24092.
285	120.7	191.8	24695.
290	121.2	193.9	25299.
295	121.6	196.0	25906.
298.16	121.8	197.2	26291.
300	122.0	198.0	26515.
305	122.4	200.0	27126.
310	122.7	202.0	27739.
315	123.0	204.0	28353.
320	123.4	205.9	28970.
325	123.7	207.8	29587.
330	124.0	209.7	30206.
335	124.3	211.6	30827.
340	124.5	213.4	31449.
345	124.8	215.2	32072.
350	125.1	217.0	32697.
355	125.3	218.8	33323.

(a) Extrapolation using Debye function $0.15396\ D\left(\frac{130.7}{T}\right)$.

$$(51)\quad H-H_{0°C} = 0.07608\ t + 1.44 \times 10^{-5}\ t^2 - 0.032 + \frac{1.3}{t+41} \qquad \text{(cal/g)}$$

$$(\pm\ 0.2\%,\ 0-427°C) \qquad (t \text{ in } °C)$$

$$(52)\quad S-S_{0°C} = 0.15706 \log_{10}T + 2.88 \times 10^{-5}\ T - 0.39062 + \frac{0.0056}{T-232}$$

$$+ 5.6 \times 10^{-5} \log_{10}\left(\frac{T-232}{T}\right) \qquad \text{(cal/g °K)}$$

$$(\pm\ 0.2\%,\ 0-427°C) \qquad (T = t + 273.16)$$

At temperatures above 100°C, the last terms in (50) and (51) and the last two terms in (52) are negligible.

To obtain values of enthalpy and entropy referred to 0°K, the values 14.64_4 cal/g and 0.1174_8 cal/(g°K) respectively, taken from Table 14, can be added to those given in Table 15 and equations (51) and (52).

TABLE 15

SPECIFIC HEAT, ENTHALPY AND ENTROPY OF SOLID URANIUM TETRACHLORIDE FROM 0° TO 427°C

T°C	C_p cal/(g °C)	$H-H_{0°C}$ cal/g	$S-S_{0°C}$ cal/(g °K)
0	0.07516	0	0
50	0.07735	3.815	0.012830
100	0.07917	7.728	0.024083
150	0.08063	11.726	0.034132
200	0.08196	15.790	0.043204
250	0.08328	19.920	0.051501
300	0.08472	24.120	0.059164
350	0.08616	28.392	0.066309
400	0.08760	32.736	0.073011
426.84 (700°K)	0.08838	35.099	0.076450

The heat of formation of UCl_4 was first determined by Biltz and Fendius (1928); this determination was repeated at Berkeley (UCRL 7). The method consisted in dissolving uranium metal and UCl_4 separately in 12 N HCl containing 10 per cent ferric chloride, and comparing the heats of solution (measured in an all-glass, Bunsen-type ice calorimeter). The acid and the ferric salt were present in such large excess that heat effects caused by concentration changes could be neglected. In the reaction of uranium metal with Fe(III) the liberated hydrogen may reduce some of the Fe(III) ions; this effect can be taken into account by determining the ferrous iron with ceric sulfate after the dissolution has been completed.

The heats of solution in combination with other known thermochemical data permit the calculation of the heat of formation of UCl_4:

$$(43) \quad U(s) + 2Cl_2(g) \longrightarrow UCl_4(s) : \quad \Delta H_{273} = -250.9 \pm 0.6 \text{ kcal/mole}$$

The earlier determination by Biltz and Fendius gave a very similar result.

The reduction equilibrium,

$$UCl_4 + 1/2\, H_2 \rightleftharpoons UCl_3 + HCl,$$

has been discussed in Section 1 of this chapter (cf. equation 1). The following values for the heat and free energy of formation of UCl_4 are derived from the experimental results given there:

$$(43a) \quad \Delta H_{298^\circ} = -251.0, \qquad \Delta F^\circ_{298} = -229.65$$

$$(43b) \quad \Delta S_{298^\circ} = -71.5$$

$$(43c) \quad \Delta H = -252{,}600 + 5.70\, T - 7.79 \times 10^{-4}\, T^2$$

$$(43d) \quad \Delta F^\circ = -252{,}600 - 13.13\, T \log T + 7.79 \times 10^{-4}\, T^2 + 109.25\, T$$

The heat of formation agrees well with that derived above by the method of Biltz and Fendius. The formation of uranium tetrachloride from UCl_3 and 1/2 Cl_2 is endothermal; therefore, with increasing temperature, UCl_4 becomes more and more stable with respect to dissociation into UCl_3 and chlorine. Calculations show that UCl_4(g) cannot be decomposed to UCl_3 at any attainable temperature under less than atmospheric pressure.

(g) Optical Properties. The red vapor of UCl_4 absorbs light between 500 and 220 mμ. Absorption becomes strong around 310 mμ and rises toward shorter wave lengths. As the concentration of the vapor increases (t = 430°C and higher), absorption spreads throughout the visible spectrum. Pressures of UCl_4 vapor as low as 3×10^{-3} mm could be detected optically in a 37.5 cm tube (UCRL 36).

The absorption spectrum of aqueous solutions of UCl_4 also has been studied (MP Chicago 6). Maxima occur at 429.5, 485, 495, 549, 649 and 672 mμ. Beer's law is obeyed at 649 mμ over the concentration range from 0.007 to 0.020 M/ℓ. The absorption spectrum of U(IV)-ions will be considered in more detail in Chapter .

(h) Electrical and Magnetic Properties.

Magnetic Susceptibility. The molecular susceptibility of UCl_4(s) has been determined as a function of the temperature by Sucksmith (1932) (Table 16). Curie's law is obeyed at low temperatures. Since Sucksmith stated that UCl_4 is unstable above room temperature, it must be concluded that no adequate precautions were taken to exclude moisture and air during the measurements. Consequently, these results are of doubtful value and are cited here only in the absence of better data.

TABLE 16

MOLECULAR SUSCEPTIBILITY OF URANIUM TETRACHLORIDE (after Sucksmith)

T°K	$\chi_{mol.} \times 10^5$	$\chi_{mol.} \times T$
90	.01058	0.952
198	488	0.965
273	413	1.130
289	410	1.185

__Electrical Conductivity.__ Molten UCl_4 was found by Hampe (1888) to be a good conductor of electricity. The specific conductivity as a function of temperature was studied by Biltz and Voight (1924). Although the measurements seem good in themselves, doubt is cast on the validity of the results by the fact that the boiling point of the UCl_4 given by them differed considerably from the value currently accepted for pure tetrachloride. Their data are presented, however, in Table 17 since no other measurements are available. Electrolytic reduction of molten UCl_4 has been utilized in the preparation of uranium metal (see Chapter 4).

TABLE 17

CONDUCTIVITY OF URANIUM TETRACHLORIDE

T°C	Conductivity in reciprocal ohms
570	0.34
598	0.42
620	0.48

2.3 Chemical Properties of Uranium Tetrachloride. Uranium tetrachloride attracts water and oxidizes in air, and should therefore be handled in a dry, inert atmosphere.

(a) Water. Uranium tetrachloride is very hygroscopic. Although less sensitive to moisture than UCl_5 or UCl_6, the tetrachloride will react when water vapor is present at a partial pressure of more than 2 mm Hg. The water absorption is not limited to the formation of a UCl_4-hydrate but proceeds further by chemical reaction with the formation of $UOCl_2$ and hydrogen chloride until it results in complete dissolution and decomposition of the tetrachloride (UCRL 37). Brown University observers found, however, that very little hydrogen chloride is evolved until sufficient water has been absorbed to form $UCl_4 \cdot 2H_2O$ (Brown 8).

Uranium tetrachloride dissolves in water with the evolution of heat to form a green solution which exhibits the characteristic properties of the U(IV)-ion (Zimmermann, 1883). The heat of solution in aqueous hydrochloric acid (1 mol HCl/8.808 mol H_2O) has been determined as 39.4 ± 0.2 kcal/mole (Biltz, 1928). Since aqueous solutions of UCl_4 always have an acid reaction, considerable hydrolysis must occur. When an attempt is made to concentrate the aqueous solution by evaporation, hydrogen chloride is evolved and a complex mixture of hydrated uranium oxides precipitates. (Consideration of the ionic species present in aqueous solutions of UCl_4 is deferred to the general discussion of the properties of U(IV)-solutions in Chapter 17).

Action of steam on UCl_4 at 600°C leads to U_3O_8.

(b) Non-aqueous Solvents. UCl_4 is generally soluble in strongly polar solvents, and insoluble in non-polar solvents such as hydrocarbons, benzene, chloroform and ether. It dissolves in certain oxygen-containing organic solvents, but solvolysis makes it impossible to recover the UCl_4 from such solutions. For example, alcoholysis occurs when UCl_4 is dissolved in methanol or ethanol (Fischer, 1913). Small amounts of water can apparently be present in alcoholic solutions without causing hydrolysis (Purdue 2). Solutions of UCl_4 in alcohol conduct electricity.

Uranium tetrachloride dissolves in acetone, probably also with chemical reaction, forming a greenish-yellow solution (Renz, 1903). Pierlé (1919) found that this solution has good electrical conductivity. Pyridine, ethyl acetate and ethyl benzoate also dissolve UCl_4 with chemical reaction.

Uranium tetrachloride is insoluble at temperatures up to 70°C in inorganic solvents such as PCl_3, $SnCl_4$ and $POCl_3$ (MP Ames 17), and also does not dissolve in liquid, anhydrous hydrogen fluoride (British 3).

(c) Oxidizing Agents. The reaction of UCl_4 with oxygen at elevated temperatures has been studied at the Tennessee Eastman Laboratories (TEC-CEW 28). The results differed from those obtained in the earlier work at Berkeley (UCRL 38). The reaction of oxygen and UCl_4 proceeds, according to the TEC-CEW investigators, in two steps:

(53) $UCl_4 + O_2 \longrightarrow UO_2Cl_2 + Cl_2$

(54) $3UO_2Cl_2 + O_2 \longrightarrow U_3O_8 + Cl_2$

The lowest temperature at which measurable reaction occurs is 230 ± 5°C for reaction (53) and 250 ± 10°C for reaction (54). No analytical data were obtained to show that the "black compound" obtained by oxidation actually was U_3O_8, although this was postulated to be the case. The energies of activation for the two reactions were estimated to be 12 kcal and 45 kcal, respectively. An examination of the kinetic data indicates that the rate determining step is the oxidation itself, and not the diffusion of the gas through the solid.

Chlorine reacts with UCl_4 at elevated temperatures to form mixtures of UCl_5 and UCl_6. (This reaction is discussed in connection with the preparation of UCl_5 in Section 3.1.) Uranium tetrachloride may also be chlorinated to a mixture of UCl_5 and UCl_6 at 115°-125°C by means of chlorine solution in CCl_4. Fluorine converts UCl_4, as it does all other uranium compounds, to UF_6. The reaction may be dangerous because of the explosive nature of chlorine fluoride which is produced in its course.

(d) Reducing Agents. Hydrogen reduces UCl_4 to UCl_3 under atmospheric pressure, at a temperature of 525°-550°C (Brown 5) (see Section 1.1a). Contrary to statements in the older literature, hydrogen bromide and hydrogen iodide also can reduce UCl_4 to the trivalent state (TEC-CEW 1) (instead of merely exchanging the halogen atoms):

$$(55) \qquad UCl_4 + 4HBr \xrightarrow{300°-350°C} UBr_3 + 4HCl + 1/2\ Br_2$$

$$(3) \qquad UCl_4 + HI \xrightarrow{350°-420°C} UCl_3 + HCl + 1/2\ I_2$$

At higher temperatures, however, HBr forms UBr_4, while HI gives mixed iodochlorides. Hydrogen fluoride always gives UF_4. Alkali metals (lithium, sodium, potassium, calcium, magnesium and aluminum) reduce UCl_4 to metallic uranium. (See Chapter 4.)

(e) Double Decomposition Reactions. Sulfides and selenides react with UCl_4 to give the corresponding U(IV)-sulfide or selenide (Colani, 1907):

(56) $$UCl_4 + 2H_2S \xrightarrow{550°C} US_2 + 4HCl$$

(57) $$UCl_4 + 2H_2Se \xrightarrow{550°C} USe_2 + 4HCl$$

In general, UCl_4 reacts at elevated temperatures with most oxygen-containing compounds to form UO_2. Silicon dioxide (quartz), SiO_2, was said not to react with molten UCl_4 (Hönigschmid, 1928), but glass has been reported to be attacked severely (Biltz, 1928a). (For more data on corrosion of quartz and glass, see Section (g).) Uranium dioxide itself reacts with molten UCl_4 to give $UOCl_2$.

(f) Complex Compounds of UCl_4. Uranium tetrachloride is co-ordinatively unsaturated and consequently forms numerous complex compounds. Gaseous ammonia is absorbed by UCl_4 at moderate temperatures to give compounds containing one, two or three moles of ammonia. Part of the ammonia taken up in this way is retained even in vacuum. Liquid ammonia forms a greenish-white compound, $UCl_4 \cdot 12NH_3$:

(58) $$UCl_4(s) + 12NH_3 \longrightarrow UCl_4 \cdot 12NH_3 + 183 \text{ kcal}$$

At 100°C, enough ammonia is lost by the latter compound to form $UCl_4 \cdot 8NH_3$. Both these compounds are unstable in air and react with water to form hydrated uranium(IV)-hydroxide. At high temperatures, a mixture of oxide and nitride results (Beck, 1932). Quinoline and pyridine form similar addition compounds with UCl_4 by reaction in acetone solution. The complex compounds separate as yellow crystals which may be recrystallized from boiling absolute alcohol (Renz, 1903).

Double salts of the type M_2UCl_6 have been prepared, where M may be Li, Na, K or R_4N. Some of these compounds found application in the electrochemical preparation of uranium metal (cf. Chapter , p.). Because of their greater stability in air, they are sometimes used also in chemical preparative work in lieu of anhydrous UCl_4. Compounds of this type cannot be prepared by precipitation from aqueous solution. The potassium compound, K_2UCl_6, may be prepared by the reaction of UCl_4 vapors with KCl at red heat (Aloy, 1899). It is a dark green crystalline material, somewhat hygroscopic in air, melting at 350°C. It can be heated to 550°C without evolution of vapors. It dissolves in water with decomposition, is soluble in alcohol and ethyl acetate and is practically insoluble in ether. The sodium and rubidium compounds are prepared in the same way and have similar properties. The existence of a lithium compound of this type is still doubtful. (See Table 18.)

TABLE 18

PHASE RELATIONSHIPS OF URANIUM TETRACHLORIDE AND VARIOUS HALIDES

System	Compound	Melting Point of Compound	Eutectic	Melting Point of Eutectic
UCl_4 - KCl	K_2UCl_6	650° ± 5°C	KCl-K_2UCl_6 (25 mole % UCl_4) K_2UCl_6-UCl_4 (53 mole % UCl_4)	560° ± 5°C 350° ± 5°C
UCl_4 - NaCl	Na_2UCl_6	Transformed to NaCl + UCl_4 at 430° ± 5°C	$2Na_2UCl_6$ - UCl_4 (50 mole % UCl_4)	370° ± 5°C
UCl_4 - LiCl	None		?	410°C and 430° ± 5°C
UCl_4 - $CaCl_2$	None		?	485° ± 5°C
UCl_4 - $BaCl_2$	Ba_2UCl_8		?	515°C 425° ± 5°C
UCl_4 - UCl_3*	None		Components insoluble in liquid phase and only slightly soluble in solid phase	

* The Ames Group reports the melting point of 11.7 mole % UCl_3 in the UCl_3-UCl_4 system to be lower by 14°C than the melting point of UCl_4.

The alkaline earths form similar double chlorides with UCl_4. Two such compounds have been prepared, namely $BaUCl_6$, and $SrUCl_6$, both resembling the potassium double salt closely. Pyridinium and quinolinium salts, $(C_5H_6N)_2UCl_6$ and $(C_9H_8N)_2UCl_6$, also are known. These can be prepared by adding pyridine or quinoline to a solution of UCl_4 in absolute alcohol saturated with hydrogen chloride (Rosenheim, 1932).

The phase relationships in systems containing UCl_4 together with a number of other halides have been studied by thermal analysis (Brown 8). The results are summarized in Table 18. No x-ray investigations of these systems have as yet been made. (See Chapter 12.)

(g) Corrosion of Various Materials by UCl_4 (TEC-CEW 2). The corrosive action of UCl_4 has received much study, but, as often in corrosion work, the results are not entirely consistent. After three hours at 465°C there appeared to be no pronounced attack by solid or gaseous UCl_4 on graphite, refractory porcelain or alundum (Princeton 1). Quartz also proved to be resistant under these conditions, although other investigators have found that it is attacked. Liquid UCl_4 definitely attacks both quartz and pyrex glass. Under identical conditions of exposure, the loss in weight of tungsten, molybdenum and nichrome was found to be less than 1 mg/cm^2; nickel, tantalum, monel and stainless steel lost 1-2 mg/cm^2, while copper is very badly attacked. When lead and tin were exposed to UCl_4 vapor, the weight losses were 9.6 per cent and 0.64 per cent respectively (UCRL 39). Exposure of a number of metals to UCl_4 vapor for five hours at 600°C gave results which are summarized in Table 19 (MP Ames 10). Samples of 18-8 stainless steel and nickel were

TABLE 19

CORROSION OF SOME METALS BY URANIUM TETRACHLORIDE VAPOR AT 600°C

Material	Weight less in 5 Hours (mg/cm^2)
Monel	5.8
Chromel A	5
18-8 Stainless Steel	22.5
Galvanized Iron	40
Copper	Very badly corroded

exposed to UCl_4 vapor at 500°C for periods of 12 to 40 hours. The corrosion expressed as g/(cm^2 hr) proved to be constant, independently of the length of the experiment. The corrosion of 18-8 stainless steel varied from 0.0001 to 0.0036 g/(cm^2 hr); that of nickel varied from 0.00012 to 0.00017 g/(cm^2 hr) (MP Ames 5). Inconel, nickel and nichrome showed negligible corrosion between 440° and 520°C. Type 304 stainless steel and Monel K undergo significant corrosion, with steel showing a higher rate of corrosion than monel below 520°C (UCRL 40).

It appears, then, that the materials most resistant to UCl_4 are nickel and nickel alloys. Copper should not be used and plated surfaces should be avoided. While some workers consider stainless steel a satisfactory material, this is by no means certain.

Some work has been done on corrosion of various metals and alloys by aqueous solutions of UCl_4. When 14K white gold, 14K yellow enamel and 20K white gold were immersed in a 0.47 M UCl_4 solution at room temperature for 24 hours, no corrosion was visible. Enamelled iron subjected to the same treatment corroded at the rate of 0.1 g/(m^2 day) (UCRL 41). "Anodized" aluminum corrodes with steadily increasing rapidity in such a solution. Welded portions of steel corroded more rapidly than the steel itself; heat treatments of 18-8 stainless steel increased the rate of corrosion thirtyfold. In stainless steels, the nickel content is an important factor; the more nickel, the less corrosion.

3. Uranium Pentachloride, UCl_5

Uranium pentachloride was discovered by Roscoe in 1874 as a by-product of the preparation of UCl_4. Subsequently, many investigators observed that higher uranium chlorides are formed when UCl_4, in the process of its preparation, is permitted to come into contact with chlorine in the heat; but not much attention was paid to these by-products. Ruff and Heinzelmann (1911) attempted unsuccessfully to use UCl_5 as an intermediate in the preparation of UF_6; but in general, the difficulties of manipulation of the pentachloride discouraged the further investigation of this compound.

The interest in UCl_5 was re-awakened when it was discovered in 1943 that this halide undergoes thermal disproportionation into tetrachloride and the formerly unknown hexachloride (UCRL 42):

$$2UCl_5 \longrightarrow UCl_4 + UCl_6. \tag{59}$$

Analysis of UCl_5 is usually performed by hydrolysis and determination of U(IV) and U(VI) in the resultant solution. If $UOCl_4$ or UO_2Cl_2 are present in the analyzed material, the value obtained for the U(VI) content will be too high.

3.1 Preparation of Uranium Pentachloride. There are two practical methods for the preparation of the pentachloride. The first consists in the treatment of the lower uranium chlorides with chlorine gas in the heat; the second, based on the work of Michael and Murphy (1910), is the liquid phase chlorination of uranium trioxide by carbon tetrachloride. The latter method has received intensive study at the

Brown University and at the Tennessee Eastman Laboratories, and offers at present the most satisfactory way for preparing UCl_5.

(a) Reaction of UCl_4 with Chlorine and CCl_4-vapor. Uranium tetrachloride can be converted to UCl_5 by the action of chlorine at 520°-555°C (UCRL 43):

$$2UCl_4 + Cl_2 \longrightarrow 2UCl_5 \tag{60}$$

The addition of small amounts of CCl_4-vapor to the chlorine stream has been advocated but does not appear to be particularly useful, especially if the starting material (UCl_4) is sufficiently pure (UCRL 44).

The Cl:U ratio in the product obtained by reaction (60) depends on the rate of cooling and may be as high as 5.5, indicating a considerably greater content of chlorine than that corresponding to the formula UCl_5. It has been suggested that compounds of the type $xUCl_6 \cdot yUCl_4$ are formed, where the ratio x:y may have values greater than one. However, it seems more likely that in these intermediary compounds, and in UCl_5 as well, all uranium atoms are equivalent and bear the same charge (compare the structure of the uranium fluorides (Chapters 11 and 12) and of U_2O_5 (Chapter 11)).

Mixtures of UCl_4 and UCl_5 can be converted to pure UCl_5 by the action of liquid chlorine at elevated temperature and pressure (Ruff, 1911). Bubbling of chlorine through UCl_4 suspended in boiling CCl_4 (76°C) does not suffice to produce UCl_5 (Brown 5).

Attempts have been made to prepare UCl_5 by reaction of uranium oxide with carbon tetrachloride vapor at 550°C in a stream of air; but the product was found to contain oxygen (as UO_2Cl_2 or $UOCl_4$) (UCRL 45). (The existence of fairly stable $UOCl_4$ has been made likely by experiments on the low temperature chlorination of UO_2Cl_2 by CCl_4 (cf. UCRL 46; this point will be discussed in greater detail in Section b).

(b) Liquid Phase Reaction of Uranium Oxides with CCl_4. As we pointed out in the section on the preparation of UCl_4, liquid phase halogenation of uranium oxides with CCl_4 can be made to yield either the tetra- or the pentachloride. Here we shall be concerned with the specific conditions under which UCl_5 is obtained.

The reaction of uranium oxides with liquid carbon tetrachloride was first studied by Michael and Murphy (1910) who found that at 250°C, UO_3 or U_3O_8 rapidly reacted with liquid CCl_4 in a sealed tube to give UCl_5 (cf. Brown 1). Lately, the behavior of boiling CCl_4 at atmospheric pressure has also been investigated. Under these conditions the reaction is much slower, 24 hours of refluxing resulting in only 10 to 30 per cent conversion. If even a small amount of UCl_5 is added at the beginning, only a short heating period is required to obtain completely water-soluble products from either UO_3 or U_3O_8. However, these products are mainly oxychlorides, and their conversion to the pentachloride proceeds only very slowly (see p. for more details).

Uranium trioxide can be converted completely to UCl_5 at 76°C (which is the boiling point of CCl_4) in 72 hours if a large excess of carbon tetrachloride (100 per cent) is used; UCl_5 must be added to the extent of 30 per cent of the weight of the oxide. Chlorine must be bubbled continuously through the boiling mixture (Brown 4,5,19). A difficulty of the liquid phase reaction at atmospheric pressure is that minute traces of acid seem to inhibit the reaction strongly (UCRL 47).

The liquid phase halogenation of uranium oxide by CCl_4 proceeds much better under elevated pressure at temperatures above the boiling point, i.e., in the way used in the original work of Michael and Murphy. Rapid reaction usually occurs between 100° and 140°C; the exact temperature at which it begins being largely dependent on the kind of oxide used. In this case again, the presence of uranium pentachloride has a strong autocatalytic effect; its probable explanation will be given below.

Important for the successful preparation of UCl_5 by liquid phase chlorination are: the nature of the oxide used, the presence of the catalyst (UCl_5), the temperature and pressure and certain other factors such as the relative amount of the CCl_4, the venting of the reactor, etc.

Nature of the Oxide. Uranium trioxide prepared by thermal decomposition of uranyl peroxide, $UO_4 \cdot 2H_2O$, is more reactive than UO_3 prepared by calcination of uranyl nitrate hexahydrate, or ammonium diuranate (Brown 18). The activity does not seem to be related to the particle size but rather to the bulk density of the material (Brown 19,20): uranium trioxide prepared from uranyl peroxide has considerably lower bulk density than the material prepared in various other ways. Commercial trioxide (prepared from uranyl nitrate) usually contains so much moisture and oxide of nitrogen as to require re-calcining at 350°C, and afterwards is considerably less reactive than the "active" UO_3 made from the peroxide. The U_3O_8 prepared from $(NH_4)_2U_2O_7$ or from uranyl oxalate has, on the other hand, been described as very reactive (UCRL 48), apparently even more so than "active" trioxide made from $UO_4 \cdot 2H_2O$ (Brown 13); but U_3O_8 prepared by ignition of UO_3 was found to be comparatively inert. Uranium dioxide does not markedly react with liquid carbon tetrachloride probably because the initial products of the reaction, $UOCl_2$ and UCl_4, are insoluble in CCl_4. A mixture of UO_2 and UO_3 in the molal ratio 1:2, however, reacts like U_3O_8 (UCRL 49).

The variable reactivity of UO_3 preparations may well be associated with the existence of various crystal modifications of this oxide of which at least five are now known (MP Chicago 7, see Chapter 11, p.).

Autocatalytic Effect of UCl_5. It was stated above repeatedly that uranium pentachloride acts as an autocatalyst in the liquid phase halogenation of UO_3. The effect of the UCl_5:UO_3 ratio on the rate of halogenation is shown in Table 20, taken from a Brown University Summary Report (Brown 21):

TABLE 20

EFFECT OF ADDED UCl_5 ON THE CHLORINATION OF UO_3 with CCl_4 IN THE LIQUID PHASE AT 100°C

UCl_5 added (grams per 150 grams UO_3)	Heating Time (hours)	Mole Ratio UCl_5:UO_3 at the End	Non-volatile Residue (per cent)
30	2	0.14	47.1
100	2	0.46	4.82
30	6	0.14	13.2
100	6	0.46	0.32

Quantities of UCl_5 of the order of 10 per cent of the weight of the UO_3 used already exert a noticeable catalytic effect. The probable function of the catalyst will be explained when the mechanism of this reaction is considered further below.

Temperature. Careful temperature control is one of the most important factors in the successful preparation of UCl_5. The reaction is usually carried out at temperatures between 100° and 160°C and pressures of less than 200 psi. It is desirable to conduct the reaction at as low a temperature as possible because this minimizes the decomposition of the UCl_5 to UCl_4 and Cl_2. Above 140°C, mixtures of UCl_5 and UCl_4 are obtained instead of pure pentachloride.

The temperature at which the reaction is initiated is of the utmost importance. The halogenation is exothermic; if the reaction mixture has to be heated to a high temperature before the reaction starts, the consequences of the subsequent, sudden evolution of heat may be disastrous. This is the principal motive for using as active an oxide as possible. With a reactive oxide, the reaction can be initiated at temperatures as low as 110°C and carried to completion at 140°C. After the reaction has started, the temperature can be controlled by permitting CCl_4 to distill from the autoclave. When the initial rapid conversion has subsided, the temperature can be raised slowly. Because the reaction may be very rapid at the beginning and may suddenly liberate a large amount of heat, precautions must be taken in designing equipment for chlorinating large amounts of UO_3 (UCRL 50).

Quantity and Quality of Carbon Tetrachloride. A large excess of CCl_4 does not change the temperature at which the reaction begins, or the duration of the first, violent phase of conversion, but it does reduce the maximum temperature reached during this phase and cuts the time required for completion of the process. Also, the product contains less non-volatile residue if excess CCl_4 is used (Brown 19). An excess of 100-300 per cent CCl_4 above the stoichiometric quantity appears appropriate (Brown 15); the larger the absolute quantity of UO_3 taken, the greater should be the excess of CCl_4. Material containing carbon disulfide in small amounts (such as 0.25 per cent) behaves as well as and perhaps even better than rigorously purified carbon tetrachloride (Brown 22; UCRL 51).

Miscellaneous Factors. The effect on the liquid phase chlorination of a long preheating period at low temperatures (80°-90°C) has been investigated in hope of achieving a better control of the reaction (Brown 15,19). Some improvement occurred in that after preheating, the first phase of the reaction was somewhat less violent, but on the whole, the results were not too satisfactory.

Moisture appears to exercise a detrimental effect on the conversion. True, workers at Brown University stated that the only effect of water is to delay the onset of the reaction and that once the reaction has started it proceeds as rapidly with moist as with dry material (Brown 15); but other investigators, basing their conclusions on extended practical experience, asserted that moisture interferes with the quality of the product and renders the yields unpredictable (UCRL 52). This is not surprising considering the known sensitivity of UCl_5 to moisture. UCl_5 yields appear to be improved by the repeated use of the same equipment without cleaning, and yields as high as 97 per cent UCl_5 can be obtained in this way (Brown 17).

To summarize, liquid phase reaction with carbon tetrachloride can be successfully used to convert the oxides of uranium directly to UCl_5 without the preliminary preparation of UCl_4. The principal difficulty lies in controlling the reaction. A better understanding of the correlation of reactivity of the oxide with its crystal structure may help in overcoming this obstacle in the future.

Mechanism of Conversion (Brown 22,23). In the interpretation of the mechanism of the liquid phase halogenation of uranium oxide with carbon tetrachloride, the following three facts must be explained:
(a) The reaction can be made to yield either UCl_4, or UCl_5 or UCl_6;
(b) UCl_5 acts as a catalyst; and (c) chlorine and phosgene are found among the products.

The over-all reactions by which CCl_4 converts UO_3 or U_3O_8 to UCl_5 with the liberation of chlorine and phosgene can be represented by the following equations:

(38) $$2UO_3 + 6CCl_4 \longrightarrow 2UCl_5 + 6COCl_2 + Cl_2$$

(61) $$2U_3O_8 + 16CCl_4 \longrightarrow 6UCl_5 + 16COCl_2 + Cl_2$$

At higher temperatures, or if phosgene and chlorine are continuously removed, UCl_5 decomposes into UCl_4 and chlorine:

(62) $$2UCl_5 \rightleftharpoons 2UCl_4 + Cl_2$$

Under these conditions the product may contain much UCl_4, or may even be pure UCl_4 (see Section 2). When extra chlorine is added to the system, not only will equilibrium (62) be shifted back to the left, but chlorination may even proceed further leading to the formation of UCl_6:

$$(63) \qquad 2UCl_5 + Cl_2 \rightleftharpoons 2UCl_6$$

Even if no extra chlorine is added, and the solvent is removed below its boiling point, a few per cent of UCl_6 is always found in the UCl_5. This may be interpreted as indicating the liberation of enough chlorine by reaction (62) to produce a small amount of UCl_6 by reaction (63). Alternatively, the same may result from direct disproportionation of two molecules of UCl_5 into UCl_4 and UCl_6.

In equations (38) and (61) it was assumed that the primary product is UCl_5. A more reasonable hypothesis, however, is that the primary product (at least with UO_3) is UCl_6:

$$(64) \qquad UO_3 + 3CCl_4 \longrightarrow UCl_6 + 3COCl_2,$$

and that all of the other uranium halides arise by thermal decomposition of the UCl_6. This will be elaborated below on p.   .

A detailed investigation has been carried out at Brown University to determine the mechanism of the autocatalytic action of UCl_5 on the reaction of UO_3 with liquid CCl_4. While UO_3 and CCl_4 alone do not react appreciably at 65°C even after ten hours, a water-soluble product is formed within three hours if UCl_5 ($2UCl_5$:$1UO_3$) is added. (Cf. above, p.   and   .) A study of the products isolated after two to sixteen hours of reaction shows a slowly progressing chlorination of the uranium.

The (completely water-soluble) solid obtained by removal of the solvent after fifteen hours of interaction was divided into four fractions on the basis of decreasing solubility in CCl_4; each fraction was analyzed by determining the Cl:U ratio and the oxygen content. (Sublimation in vacuum at 750°C leaves a residue of UO_2, the amount of which is proportional to the oxygen content of the investigated fraction.) The results showed fairly conclusively that the water-soluble solid consisted of UCl_5 (soluble in CCl_4), $UOCl_4$ (somewhat soluble), $UOCl_3$ (less soluble) and UO_2Cl_2 (insoluble).

The intermediate formation of the oxychlorides having thus been established, the autocatalytic effect of UCl_5 can be explained by the assumption that reaction first occurs between UO_3 and UCl_5 which gives oxychlorides. The latter then undergo chlorination by CCl_4 more readily than does UO_3 itself. A likely mechanism for the first step is:

(65) $$UO_3 + UCl_5 \longrightarrow UOCl_3 + UO_2Cl_2$$

(66) $$UO_2Cl_2 + UCl_5 \longrightarrow UOCl_3 + UOCl_4$$

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(67) $$UO_3 + 2UCl_5 \longrightarrow 2UOCl_3 + UOCl_4$$

Chlorination of the intermediates by CCl_4 can then occur according to the equations:

(68) $$2UOCl_3 + 2CCl_4 \longrightarrow 2UCl_5 + 2COCl_2$$

(69) $$UOCl_4 + CCl_4 \longrightarrow UCl_6 + COCl_2.$$

The overall reaction will then be

(70) $$UO_3 + 2UCl_5 + 3CCl_4 \longrightarrow 2UCl_5 + UCl_6 + 3COCl_2.$$

One mole UCl_6 should thus be present in the final product for each two moles UCl_5 added, unless the conditions are such that UCl_6 decomposes into UCl_5 and chlorine. The conditions specified for the preparation of UCl_5 usually assure complete decomposition of UCl_6 (or of its precursor, $UOCl_4$); conditions for obtaining UCl_6 as final product will be discussed in Section 4.1. This mechanism indicates why the ratio $2UCl_5$ per 1 UO_3 is necessary to obtain complete conversion at the fastest possible rate.

The thermal stability of the above-postulated intermediate oxychlorides has been investigated in a qualitative way. The mixture of water-soluble reaction intermediates was found to evolve chlorine readily at 130°C, and a measurable amount of chlorine was obtained even at temperatures as low as 88°C. Since UCl_5, as well as UCl_6, gives off only traces of chlorine at 130°C (under atmospheric pressure), the source of the chlorine must be the decomposition of the intermediates. However, the $UOCl_3$ fraction obtained from the crude mixture by elution with CCl_4 was found to be surprisingly stable; its decomposition occurred only above 375°C. The low temperature decomposition is therefore best explained by the reaction,

(71) $$UOCl_4 \longrightarrow UOCl_3 + \tfrac{1}{2}Cl_2$$

The high thermal stability of $UOCl_3$ stops the decomposition of $UOCl_4$ before $UOCl_2$ is reached.

The chlorination of UO_3 by liquid $SOCl_2$ and UCl_5 probably follows the same course as the reaction with CCl_4.

3.2 Physical Properties of UCl_5. Few of the physical properties of this compound have been studied. As prepared by reaction of UCl_4 with chlorine, it usually is a red-brown, microcrystalline powder. High pressure autoclave preparations are reddish-black crystals with a metallic luster. Attempts have been made to re-crystallize the red-brown microcrystals of UCl_5 from CCl_4 solution in an autoclave, but these attempts have been unsuccessful (UCRL 53).

(a) Density. A density determination by direct displacement in benzene gave a value of 3.81 g/cc (MP Ames 18). The packing density of autoclave-prepared material is 1.95 g/cc (UCRL 54).

(b) Melting Point and Volatility. Since UCl_5 undergoes both thermal decomposition and disproportionation, no accurate values for the melting point or volatility are available. The vapor pressure has been estimated to be 10^{-7} mm Hg at 50°C; because of disproportionation, doubts have been expressed concerning the possibility of UCl_5 existing as a vapor above 60°C (UCRL 55). At Brown University it was found impossible to separate UCl_5 and UCl_6 by sublimation and this was interpreted as indicating a rather high volatility of the pentachloride. UCl_5 can be distilled in an atmosphere of chlorine containing some CCl_4, but the sublimate is enriched in UCl_6 (UCRL 56).

(c) Molecular Weight (TEC-CEW 29). The molecular weight of UCl_5 has been determined by ebullioscopy in carbon tetrachloride solution. It was found to correspond quite closely to a dimer $(UCl_5)_2$. It may thus be suggested that UCl_5 should be formulated as U_2Cl_{10}.

(d) Thermochemistry (UCRL 4). The heat of formation of UCl_5 has been determined at Berkeley by measuring the difference in the heats of solution of UCl_4 and UCl_5 in water containing excess $FeCl_3$.

$$(72)\quad UCl_4(s) + 2FeCl_3(aq) + 2H_2O(\ell) \longrightarrow UO_2Cl_2(aq) + 4HCl(aq) + 2FeCl_2(aq)$$

$$\Delta H = -24.1 \text{ kcal/mole}$$

$$(73)\quad UCl_5(s) + FeCl_3(aq) + 2H_2O(\ell) \longrightarrow UO_2Cl_2(aq) + 4HCl(aq) + FeCl_2(aq)$$

$$\Delta H = -33.9 \text{ kcal/mole}$$

$$(74)\quad FeCl_2(aq) + \tfrac{1}{2}Cl_2(aq) \longrightarrow FeCl_3(aq)$$

$$\Delta H = -21.0 \text{ kcal/mole}$$

Therefore:

$$(75)\quad UCl_4(s) + \tfrac{1}{2}Cl_2(aq) \longrightarrow UCl_5(s) \qquad \Delta H = -71.2 \text{ kcal}$$

and using equation (43):

$$(75a)\quad U(s) + 5/2\ Cl_2(g) \longrightarrow UCl_5(s) \qquad \Delta H_{273} = -262.1\ (\pm 0.6) \text{ kcal/mole}$$

The entropy of UCl_5 has been estimated to be $S_{298}° = 57.0$ e.u.; ΔS for (75) then becomes -88.3 e.u. and $\Delta F°_{298} = -235.7 \pm 2.0$ kcal (UCRL 57).

(e) The dielectric constant of solid UCl_5 is 1.9 and does not vary appreciably with the frequency (TEC-CEW 30).

3.3 Chemical Properties of UCl_5.

(a) Effect of Solvents. Uranium pentachloride is very hygroscopic. It is sensitive to moisture when the partial pressure of water is 0.007 mm or more (Brown 18). Liquid water decomposes it immediately:

$$2UCl_5 + 2H_2O \longrightarrow UCl_4 + UO_2Cl_2 + 4HCl \tag{76}$$

To avoid loss of hydrogen chloride when this reaction is used for analytical purposes, it is advisable to add the UCl_5 to dilute sulfuric acid cooled to -78°C and to allow the reactants to warm up slowly (Brown 24).

The solubility of UCl_5 in a large number of organic solvents has been examined. The solubility in CCl_4 is given in Table 21 as a function of temperature. Table 21 shows that the addition of Cl_2 decreases the

TABLE 21*

SOLUBILITY OF URANIUM PENTACHLORIDE IN CARBON TETRACHLORIDE

Temperature (°C)	g UCl_5/100 g UCl_4	g UCl_5/100 g (87.5% CCl_4 + 12.5% Cl_2)
-20	--	0.26
-16	0.29	--
0.0	0.45	0.43
22.8	0.94	--
25.0	1.04	0.82
70	5.3	
160	20 (estimated)	

* (Brown 9,19,23).

solubility of UCl_5 in CCl_4.

A number of miscellaneous observations on solubility are summarized in Table 22.

TABLE 22*

SOLUBILITY OF URANIUM PENTACHLORIDE IN VARIOUS SOLVENTS

Solvent	Solubility	Remarks
Thionyl chloride	sol	Reddish-brown solution
Pyridine	sl. sol.	Appears to form a complex
Benzotrichloride	sol. at first, but black solid forms on standing or refluxing	
$\beta\beta'$ Dichloroethyl ether	somewhat sol.	Green solution
Tetralin	sl. sol.	
Tetrachloroethane	sol.	Ppt. forms on refluxing
Tetrachloroethylene	sol. 22°C - 9% 120°C - 25%	Dark brown solution
Benzene, xylene	No solution	No reaction
Freon 11, Freon 21	Rapid reaction with Cl_2 evolution	
Freon 113	sol.	Ppt. forms on boiling

---

* (UCRL 58).

Dimethyl ether reacts vigorously with UCl_5 to form an orange, water-soluble substance. Diethyl ether, acetone, ethyl acetate, formamide, dioxane and alcohols also react immediately; chloroform, acetophenone and chlorobenzene react more slowly. No reaction is observed with isopropyl ether (MP Ames 1; Brown 23). Uranium pentachloride is highly soluble in carbon disulfide and thionyl chloride.

(b) Oxidation Reactions. Oxygen reacts with UCl_5 to give a mixture of uranium oxyhalides. Chlorine partially converts UCl_5 to UCl_6 at elevated temperatures. The reaction,

$$2UCl_5 + Cl_2 \rightleftharpoons 2UCl_6 \tag{63}$$

is reversible, but practically complete conversion of UCl_5 to UCl_6 can be obtained by treatment with chlorine in CCl_4 vapor (Brown 6). This reaction will be discussed in Section 4 of this chapter. Fluorine gas converts UCl_5 to UF_6.

(c) Double Decomposition Reactions. Liquid, anhydrous hydrogen fluoride converts UCl_5 to UF_5:

$$UCl_5 + 5HF \longrightarrow UF_5 + 5HCl \tag{77}$$

(See Chapter 12.)

(d) Reduction Reactions. Sodium metal reduces UCl_5 to metallic uranium. Uranium pentachloride is not, however, a particularly suitable source of uranium metal (Hunter, 1923). Chloroform reduces UCl_5 to UCl_4 (UCRL 59). This reduction can be carried out at 140°C in an autoclave but is of little practical value since the UCl_4 obtained is contaminated with hexachlorethane. Uranium pentachloride can be dechlorinated by refluxing with S_2Cl_2, $SnCl_4$, hexachloropropene, etc., but it is usually difficult to free the product from the solvent.

(e) Disproportionation and Thermal Decomposition. When UCl_5 is heated, it undergoes the decomposition (Roscoe, 1874):

$$(62) \qquad 2UCl_5 \rightleftharpoons 2UCl_4 + Cl_2$$

Some decomposition occurs below 100°C; at 250°C it is rapid and its rate is about the same in atmospheres of chlorine or pure nitrogen (Brown 18), indicating that the reaction is not markedly reversible under these conditions. At the Tennessee Eastman Laboratories it has been reported that UCl_5 evolves noticeable amounts of Cl_2 at 75°C and that the rate of decomposition increases rapidly at 175°C (TEC-CEW 31).

The thermal stability of UCl_5 has been studied by Martin and Eldau (1943). These workers were apparently unaware of the existence of UCl_6 and an examination of their experimental procedure indicates that their results probably refer to a mixture of UCl_5 and UCl_6 rather than to pure UCl_5. The kinetics of the thermal decomposition have been investigated at Berkeley (UCRL 55). The reaction appears to be first order with respect to UCl_5. The rate constant of reaction (62) was found to be of the order of 10^{-5}/minute for the temperature range 100°-152°C, and the activation energy was computed to be 28 kcal/mole.

In addition to thermal decomposition, UCl_5 also undergoes disproportionation:

$$(59) \qquad 2UCl_5 \longrightarrow UCl_4 + UCl_6$$

at 100°-175°C in a high vacuum. Uranium pentachloride should not be formulated $UCl_4 \cdot UCl_6$ because of this reaction. Very likely, as in the case of UF_5, all the uranium atoms in the solid are equivalent. The details of the thermal disproportionation of UCl_5 to UCl_4 and UCl_6 will be discussed in Section 4 of this chapter.

(f) Complex Compounds of UCl_5. It has been reported that a double salt $UCl_5 \cdot PCl_5$ is formed by reactions of UO_3 and PCl_5 at 180°-190°C in a sealed tube (Cronander, 1873). After removal of $POCl_3$, the double salt remains as a yellow-red, amorphous mass which melts without decomposition. It is reduced by hydrogen to HCl and PH_3; fusion with KCl gives UCl_4, PCl_5 and chlorine. Water precipitates U(IV) phosphate and forms UO_2^{++}. A closer study of this complex would be of interest.

4. Uranium Hexachloride, UCl_6

Before the preparation of uranium hexachloride, uranium hexafluoride was the only known oxygen-free hexavalent uranium compound. Uranium hexachloride was discovered as a result of the observation that initially pure UCl_5 could not be completely sublimed unless the temperature was high enough to cause the sublimation of UCl_4 as well; when sublimation was carried out below 550°C, a residue with a composition close to UCl_4 always remained (UCRL 42). The sublimate could be re-sublimed repeatedly in vacuum, or in an atmosphere of nitrogen or chlorine without leaving any further residue. Analysis of the sublimate showed it to be UCl_6 and it became clear that it must arise by disproportionation of UCl_5:

$$(59) \qquad 2UCl_5 \rightleftharpoons UCl_4 + UCl_6.$$

The rather unexpected stability of the hexachloride, coupled with its marked volatility, has aroused considerable interest. Methods of preparation have been intensively studied and some progress has been made in the examination of the physical and chemical properties.

4.1 Preparation of Uranium Hexachloride. Three methods are known for the preparation of UCl_6: (a) The above-mentioned disproportionation of UCl_5 in vacuum. The maximum amount of UCl_6 obtainable in this way is 54.6 per cent of the weight of UCl_5. (b) Reaction of UCl_4 or UCl_5 with chlorine gas at elevated temperatures. Products with a chlorine:uranium ratio up to 5.8:1 can be obtained in this way. They can be used as material for the preparation of pure UCl_6 by fractionation. (c) Reaction of a lower chloride (usually UCl_5), or of UO_3 with a mixture of chlorine and carbon tetrachloride in the liquid phase. The last method also does not yield pure UCl_6 directly; further treatment is necessary to remove the UCl_5 with which the product is mixed.

(a) Preparation of UCl_6 by Disproportionation of UCl_5 (MP Ames 4). The preparation of UCl_6 by sublimation of UCl_5 in vacuum can be carried out in a glass vessel, or a stainless steel vessel, equipped with a condenser cooled with solid CO_2. The purity of the UCl_6 obtained depends to a considerable extent on the composition of the starting material. The higher the chlorine:uranium ratio in the material used, the fewer fractional sublimations will be required to obtain pure UCl_6 (MP Ames 1,19). The necessity for repeated fractionation arises from the fact that UCl_5 itself possesses an appreciable vapor pressure (Brown 25,26,27) (UCRL 60).

Various workers have utilized disproportionation temperatures ranging from 80°C to 240°C (UCRL 54). Although the rate of sublimation increases with increasing temperature of the charge, temperatures above 150°C are better avoided in order to minimize the co-distillation of UCl_5. The disproportionation is best carried out at 120°-150°C under pressures of the order of 10^{-4} mm (UCRL 61). The closer the composition of the starting charge corresponds to UCl_5, the lower must the temperature be kept to avoid losses of the pentachloride. Since low operating pressures favor the disproportionation, a good vacuum is essential. A large capacity pumping system should be used capable of maintaining a high vacuum even when gases are continuously evolved by the reacting mass.

(b) Preparation of UCl_5-UCl_6 Mixtures by High Temperature Vapor-Phase Chlorination. When UCl_4 is treated with chlorine at elevated temperatures, mixtures of UCl_5 and UCl_6 result.

(See equation 29) $UCl_4 + \frac{1}{2}Cl_2 \longrightarrow UCl_5$

(See equation 63) $\underline{UCl_5 + \frac{1}{2}Cl_2 \longrightarrow UCl_6}$

(78) $UCl_4 + Cl_2 \longrightarrow UCl_6$

These reactions proceed at temperatures above 350°C and the composition of the product depends to a considerable extent on the rapidity with which the reaction products are cooled (Brown 18). The more rapid the cooling, the higher the UCl_6 content. The chlorine:uranium ratio in the product is higher at 350°C than at 450°C (Brown 20). Experiments showed that the sometimes suggested addition of CCl_4 vapor to the chlorine is not particularly beneficial. At the above-given temperatures a product consisting of 30 per cent UCl_6 and 70 per cent UCl_5 can be obtained.

It is often more convenient to use directly UO_3 (or other oxides) for the preparation of UCl_6 instead of utilizing UCl_4 as the intermediary. This may be achieved by chlorinating UO_3 with a mixture of chlorine and CCl_4 vapor. This reaction was discussed in the section dealing with the preparation of UCl_4 (cf. p.   ), and conditions were specified there which lead to the minimum yield of UCl_5. Now, we are interested in conditions suitable to achieve practically complete conversion to UCl_5 and UCl_6. This is accomplished by greatly increasing the proportion of chlorine. The reaction is usually carried out at 550°C. A molal ratio of at least 15 Cl_2:1 CCl_4 is desirable for maximum enrichment in UCl_6. However, a marked increase in the rate is observed with increasing partial pressure of CCl_4, which suggests that the minimum proportion of chlorine sufficient for good conversion should be used. This reaction has also been applied to a number of uranium compounds other than UO_3, with results which are summarized in Table 23 (UCRL 44,62).

The presence of small amounts of moisture in the UO_3 seemed to have no effect on the yield of UCl_6. Uranium trioxide and U_3O_8 give identical yields, which suggests that the UO_3 is first converted to U_3O_8 at the temperature of the reaction. The chlorination of U_3O_8 usually produces 67 mole per cent of UCl_6 and 33 mole per cent UCl_4, or 79.5 per cent UCl_6 by weight. The chlorination may also be carried out by treating an intimate mixture of UO_3 and carbon with chlorine at 540°C. The product so obtained has a chlorine:uranium ratio >5, but smaller than that achieved by the $UO_3 + Cl_2 + CCl_4$ reaction (UCRL 63).

TABLE 23

VAPOR PHASE CONVERSION OF URANIUM COMPOUNDS TO URANIUM HEXACHLORIDE

$Cl_2:CCl_4 = 15:1$ T = 550°C

Reactants	% Conversion to UCl_6 (Including UCl_6 obtainable from the UCl_5 produced)
$UO_2 + Cl_2 + CCl_4$	79.4
$UCl_4 + Cl_2 + CCl_4$	58.9
$UCl_4 + Cl_2$	69.7
$UO_2Cl_2 + Cl_2 + CCl_4$	78.5

An interesting feature of these reactions is that UCl_6, which is thermally unstable, can be prepared at very high temperatures, probably because it decomposes only slowly in the vapor phase. The UCl_6-vapor is quickly swept out of the hot region of the reactor by the vigorous stream of chlorine.

(c) Preparation of UCl_5-UCl_6 Mixtures by Liquid Phase Reactions. Attempts have been made to convert UCl_4 to UCl_6 by treatment with chlorine in CCl_4 solution (Brown 28,29). UCl_4 reacts very slowly with a 7 to 10 per cent chlorine solution in CCl_4 at 115°C. At higher temperatures (160°-170°C) the reaction is more rapid and chlorination to higher chlorides is practically complete after three hours. The addition of UO_3 or UCl_5 to the reaction mixture accelerates the chlorination. Uranium pentachloride and hexachloride have been produced in approximately equivalent amounts by this method. This reaction did not find much use because of its relative slowness and because so large an amount of UCl_5 is produced.

If pure uranium pentachloride is available as starting material, UCl_6 can be produced from it by the same reaction. A serious difficulty here is the erratic nature of the reaction. The rate of the reaction is sometimes very small for no obvious reason. The rate of production of UCl_6 decreases sharply with decreasing concentration of UCl_5. Therefore, a large excess of solid UCl_5 is used, thus maintaining a saturated solution of UCl_5 at all times. The chlorine concentration used is usually about 10 per cent by weight of the CCl_4. The concentration of chlorine seems to have only a minor effect on both the rate and final concentration of UCl_6 in the solution. Since solutions of UCl_6 more concentrated than 10 to 11 per cent are unstable, the reaction must be stopped when this concentration is reached. At 115°C this can usually be achieved in four hours. The rate of production of UCl_6 varies from 12 to 50 gm UCl_6/kg CCl_4/hour, and it is this unpredictability which limits the usefulness of the reaction. In an effort to determine the reason for this behavior various types of CCl_4 have been examined. It appears that technical grade CCl_4, containing small amounts of CS_2, is better than highly purified CCl_4, but this is not certain.

This process has been operated in semicontinuous form. A large excess of UCl_5 is used at the beginning. After reaction has proceeded to the point where 10 per cent UCl_6 has been formed, a portion of the solution is removed. The autoclave is then re-charged with more CCl_4+Cl_2 and the process repeated (Brown 22,23,29). The chief advantages of this procedure are that no control problems are involved and operating pressures are relatively low.

The most satisfactory method for preparing UCl_6 by liquid phase reaction consists of the treatment of UO_3 with a CCl_4+Cl_2 mixture in the presence of UCl_5 as a catalyst. In the absence of UCl_5, the reaction is unsatisfactory (Brown 9). The rate and degree of conversion of UO_3 as a function of UCl_5 concentration have been studied (Brown 23, 29,30) and the conclusion was that the initial UCl_5 concentration should be at least equal or, preferably, double that of the UO_3. When the molal ratio UCl_5:UO_3 drops below one, incomplete conversion of the UO_3 results. (The use of UCl_5 as a promoter finds a rational explanation in the mechanism for the reaction $UO_3 + 2UCl_5 + CCl_4$ which has been discussed in Section 3 of this chapter.)

The effect of chlorine concentration has also been studied. If the chlorine concentration is above 12 per cent (of the weight of CCl_4 used), then not only the UO_3 but part of the UCl_5 promoter is converted to UCl_6. Below 7 per cent the conversion of the oxide to UCl_6 is incomplete. A concentration of about 10 per cent therefore appears as the optimum. The amount of UO_3 used in the reaction is determined by the consideration that solutions of UCl_6 in CCl_4 exceeding 10 per cent are unstable. The quantities of reactants are so chosen that a 10 per cent solution results when all of the UO_3 has reacted. The reaction is best carried out at 100°-115°C. The full yield of UCl_6 is obtained at the end of 0.5 hour at this temperature, but the UO_3 is found to be incompletely deoxygenated (Brown 31), i.e., some of the UCl_5 which was used up is replaced by oxyhalides. Heating for one to three hours is therefore recommended. The reaction is carried out in a stainless steel autoclave.

A typical charge is: 363 g UO_3, 1053 g UCl_5, 530 g Cl_2 and 5150 g CCl_4. After heating for three hours at 115°C, the reactor is cooled to 35°C and about 3700 g of solution removed. The UCl_6 content of the solution is determined and the reactor is then re-charged with Cl_2, CCl_4 and an amount of UO_3 equivalent to the UCl_6 withdrawn. Under these operating conditions there is no build-up of UCl_5 in the reactor even after a number of consecutive runs (Brown 9,20,26,30,32).

The reaction of UO_3 with $2UCl_5 + CCl_4 + Cl_2$ yields a solution of about 85 per cent UCl_6 and 15 per cent UCl_5. The solubility of UCl_6 in CCl_4 is much greater than that of UCl_5 (see below). At 37°C, 100 g of solvent will dissolve 11.7 g UCl_6 and 2.1 g UCl_5 (Brown 28). The product is recovered by removing the solvent. Since the stability of UCl_6 in CCl_4 decreases markedly with increasing temperature (40 to 50 per cent of the UCl_6 may decompose to UCl_5 at 77°C), it is necessary to remove the solvent in a chlorine, or chlorine-air stream at 77°C. The solid so obtained is then sublimed in vacuum to obtain pure UCl_6 (Brown 23).

(d) <u>Purification of UCl_6</u>. Pure, anhydrous UCl_6 can be sublimed at 75°-100°C in a vacuum of 10^{-4} mm. UCl_6 is ordinarily purified by repeated vacuum sublimation but it can also be distilled in a stream of inert gas of low pressure. The product obtained by subliming UCl_6 in a stream of argon at one to two cm pressure is crystalline, and has been claimed to be purer than the product obtained by vacuum sublimation (MP Ames 10). Sublimation in chlorine or nitrogen at 350°C, however, appears to be unsatisfactory. When chlorine is used, large amounts of chlorine are absorbed which cannot be removed even by prolonged passage of inert gas over the product (UCRL 64). The effect of traces of CCl_4 on the sublimation of UCl_6 also has been studied (UCRL 65). After solution in CCl_4 or exposure to CCl_4-vapor the sublimation of UCl_6 is never complete, and a residue which cannot be sublimed at 100°C always remains.

4.2 Physical Properties of UCl_6. Uranium hexachloride forms fine, black or dark green crystals. The exact appearance depends on the method of purification and the rate at which the crystals are grown.

(a) Melting Point (UCRL 66). Despite thermal instability, it has been found possible to determine the melting point of UCl_6. The measurement was performed by immersing thin-walled tubes containing UCl_6 in an oil bath pre-heated to various temperatures. At atmospheric pressure a liquid phase is formed momentarily at 177.5 ± 2.5° C. The equilibrium pressure of chlorine caused by the decomposition,

$$UCl_6 \longrightarrow UCl_4 + Cl_2, \qquad (79)$$

must be quite high at that temperature, as judged by the very rapid disappearance of liquid UCl_6.

(b) X-ray Structure and Density (MP Chicago 5,8). Crystalline UCl_6 has been examined by x-ray methods and found to possess an hexagonal unit cell:

$$a_1 = 10.90 \pm 0.05A \qquad a_3 = 6.03 \pm 0.03A$$

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There are three molecules per unit cell and the three uranium atoms are in the following positions:

$$1\ U_I \text{ at } (0,\ 0,\ 0), \qquad 2\ U_{II} \text{ at } \pm\ (1/3, 2/3,\ 1/4)$$

The chlorine positions are still unknown.

The density computed from the x-ray data is 3.59 g/cc. A direct measurement by immersion in benzene has given a value of 1.56 g/cc (MP Ames 19) but measurements in tetrahydronaphthalene gave 3.36 ± 0.17 g/cc (UCRL 67). The packing density is about 1.75 g/cc (UCRL 68).

(c) Vapor Pressure of UCl_6. The vapor pressure of UCl_6 has been determined by two independent methods. The results obtained are not in good agreement. One set of measurements was made with an all-glass clicker gauge (UCRL 69); the vapor pressure and free energy of sublimation could be expressed to within one per cent or better by the equations:

$$(80) \qquad \log_{10} p = \frac{-2422}{T} + 6.633_7 \qquad (0\text{-}200°C)$$

$$(81) \qquad \Delta H_{\text{subl.}} = 11,120 \text{ cal/mole}$$

$$(82) \qquad \Delta F^\circ = 17,500 + 36.85\ T \log T - 129.0\ T$$

Values of the vapor pressure computed from this formula (80) are given in Table 24.

TABLE 24

VAPOR PRESSURE OF URANIUM HEXACHLORIDE, CLICKER GAUGE METHOD

Temperature (°C)	Pressure (mm Hg)	Temperature (°C)	Pressure (mm Hg)
0	0.005	120	2.95
20	0.023	140	5.75
40	0.08	160	11.07
60	0.22	180	18.60
80	0.59	200	32.35
100	1.35		

The vapor pressure of UCl_6 has also been determined by a transpiration method using purified helium gas (MP Ames 4,20). The results were corrected for evolution of chlorine arising from decomposition of the UCl_6. The vapor pressures are considerably lower than those obtained by the clicker gauge method. (Table 25)

TABLE 25

VAPOR PRESSURE OF URANIUM HEXACHLORIDE, TRANSPIRATION METHOD

Temperature (°C)	Pressure (mm Hg)
75.5	0.06
98.5	0.24
120.0	0.89
138.0	1.75

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The experimental data from the transpiration method can be represented by the following equation:

$$\log_{10} p = \frac{-3788}{T} + 9.52 \qquad (83)$$

$$\Delta H_{\text{subl.}} = -17{,}300 \text{ cal/mole} \qquad (84)$$

The values obtained by the transpiration method are probably more accurate in principle than the clicker gauge values. In the latter case no correction was made for thermal decomposition of the UCl_6, which will necessarily give rise to high results. However, the workers using the clicker gauge reported only negligible decomposition below 130°C, whereas the transpiration method workers found decomposition at practically all temperatures. Before any final conclusions can be drawn, it will be necessary to obtain comparative measurements on the same sample.

(d) Thermochemical Data. The specific heat, entropy and enthalpy of UCl_6 from 0° to 350°K have been determined by the National Bureau of Standards (5) (Table 26). $S_{298°}$ is found to be 68.28 e.u.

The heat of formation of UCl_6 has been determined at UCRL (4).

$$UCl_4(s) + 2FeCl_2(aq) + 2H_2O(\ell) \rightarrow UO_2Cl_2(aq) + 4HCl(aq) + 2FeCl_2(aq) \qquad (85)$$

$$\Delta H = -24.1 \text{ kcal/mole}$$

$$UCl_6(s) + 2H_2O(\ell) \rightarrow UO_2Cl_2(aq) + 4HCl(aq) \qquad (86)$$

$$\Delta H = -44.7 \text{ kcal/mole}$$

$$2FeCl_2(aq) + Cl_2(g) \rightarrow 2FeCl_3 \qquad (87)$$

$$\Delta H = -42.0 \text{ kcal/mole}$$

TABLE 26

SPECIFIC HEAT, ENTROPY AND ENTHALPY OF URANIUM HEXACHLORIDE(a)

FROM 0° TO 350°K

T (°K)	C (Int. joules/mole °K)	S (Int. joules/mole °K)	$H-E_0^s$ Int. joules/mole
0	0.0	0.0	0.0
5	0.793(b)	0.264	0.991
10	6.01	2.078	15.52
15	15.66	6.26	68.78
20	25.18	12.08	171.0
25	34.35	18.68	319.9
30	43.51	25.76	514.6
35	52.18	33.12	754.1
40	60.33	40.63	1,036
45	67.73	48.17	1,356
50	74.53	55.66	1,712
55	80.74	63.06	2,100
60	86.37	70.33	2,518
65	91.46	77.45	2,963
70	96.01	84.40	3,432
75	100.2	91.16	3,923
80	104.6	97.77	4,435
85	108.6	104.23	4,968
90	112.0	110.54	5,519
95	115.3	116.69	6,088
100	118.4	122.68	6,672
105	121.3	128.53	7,271
110	124.2	134.24	7,885
115	126.9	139.82	8,513
120	129.6	145.28	9,154
125	132.1	150.62	9,808
130	134.4	155.85	10,475
135	136.8	160.96	11,153
140	139.0	165.98	11,842
145	141.0	170.89	12,542
150	143.0	175.71	13,252
155	144.8	180.42	13,972
160	146.5	185.05	14,700
165	148.1	189.58	15,437
170	149.6	194.03	16,181
175	151.1	198.39	16,933
180	152.5	202.66	17,692
185	153.8	206.86	18,4 8
190	155.1	210.98	19,230
195	156.4	215.02	20,009
200	157.6	219.00	20,794

TABLE 26 (CONT'D)

T (°K)	C (Int. joules/mole °K)	S (Int. joules/mole °K)	$H-E_0^s$ (Int. joules/mole)
205	158.7	222.90	21,585
210	159.8	226.74	22,381
215	160.9	230.51	23,183
220	161.9	234.23	23,990
225	163.0	237.88	24,802
230	164.0	241.47	25,619
235	164.9	245.01	26,442
240	165.9	248.49	27,269
245	166.8	251.92	28,100
250	167.7	255.30	28,936
255	168.6	258.62	29,777
260	169.5	261.91	30,622
265	170.4	265.14	31,472
270	171.2	268.34	32,326
275	172.1	271.48	33,184
280	172.9	274.59	34,046
285	173.7	277.66	34,912
290	174.5	280.69	35,783
295	175.2	283.68	36,657
298.16	175.7	285.54	37,212
300	176.0	286.63	37,535
305	176.7	289.54	38,417
310	177.5	292.42	39,303
315	178.2	295.27	40,192
320	178.9	298.08	41,084
325	179.7	300.86	41,981
330	180.5	303.61	42,882
335	181.3	306.33	43,786
340	182.1	309.02	44,694
345	182.9	311.69	45,607
350	183.8	314.33	46,524

(a) The UCl_6 contained 6.3 per cent UCl_4; the appropriate corrections were made.

(b) Extrapolated using Debye function, 58.17 D $(\frac{89.4}{T})$.

Therefore,

$$(88) \quad U(s) + 3Cl_2(g) \rightarrow UCl_6(s) ,$$

$$\Delta H_{273} = -272.3 \pm 0.7 \text{ kcal/mole}$$

$$\Delta F^{\circ}_{298} = -241.4 \pm 1.0 \text{ kcal/mole}$$

(e) Optical Properties (Columbia 1,2). The absorption spectrum of the uranium hexachloride vapor is difficult to study because of the low vapor pressure. The absorption spectrum has been examined at 76.5°C and at 100°C using a 50 cm long tube. A weak continuous absorption band at 20,000 cm^{-1} was found. A much stronger band appeared at 27,000 cm^{-1} obviously corresponding to the absorption band of UF_6. The absorption spectrum of solid UCl_6 films at 77°K was also investigated. As would be expected, the band structure is more pronounced at the lower temperature. A sequence of rather diffuse bands are found at 20,000 cm^{-1}; below 17,000 cm^{-1} the bands become weaker, but sharper. The ultraviolet spectrum below 30,000 cm^{-1} was not investigated.

The absorption spectrum of UCl_6 in a fluorocarbon solution is shown in Fig. 2, and appears qualitatively to resemble the absorption spectrum of UCl_6 vapor.

4.3 Chemical Properties of UCl_6. Little is known about the chemical properties of UCl_6. It is extremely unstable in the presence of moist air and must therefore be handled either in a vacuum apparatus or in a good dry box. Uranium hexachloride reacts violently with liquid water to form UO_2Cl_2.

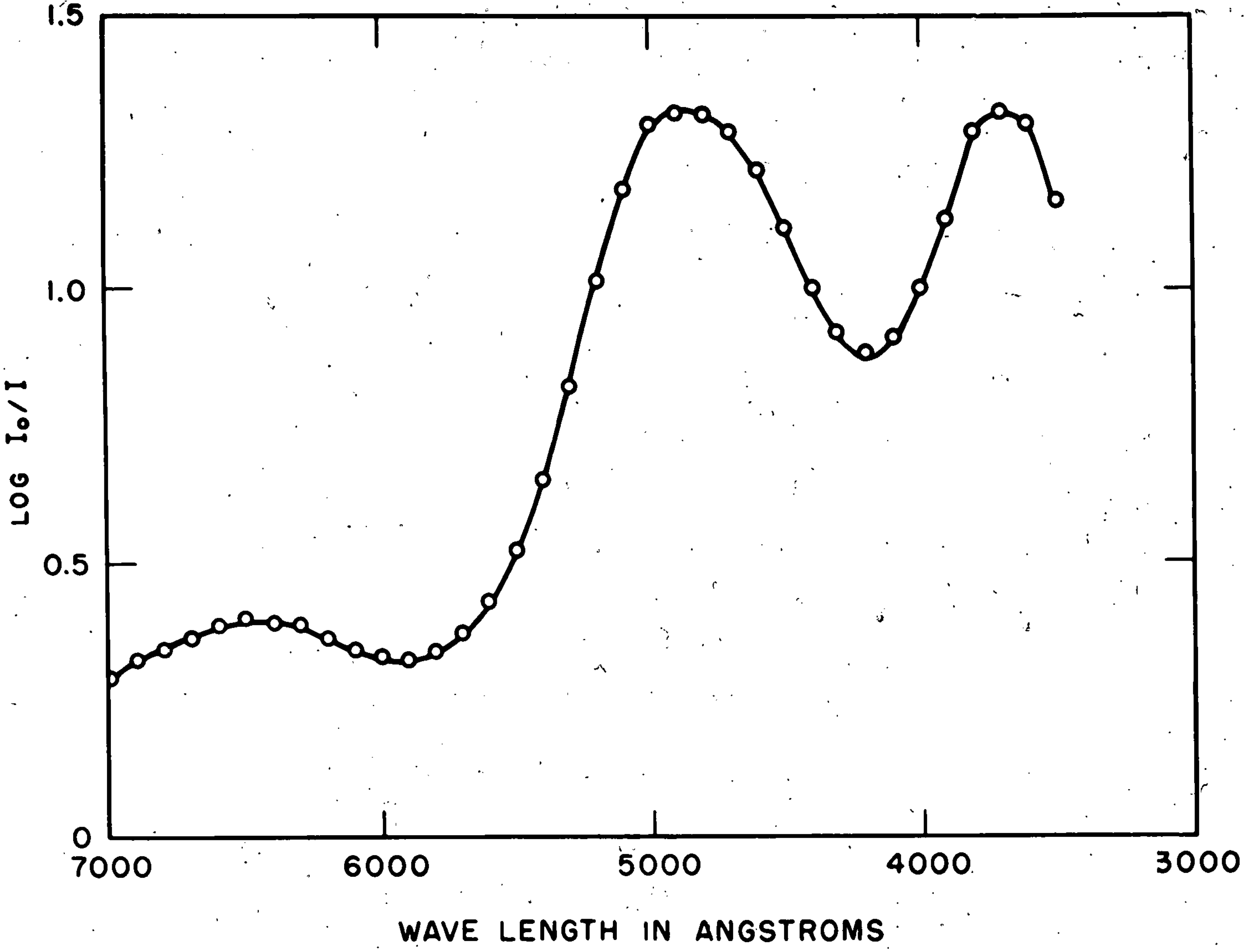

FIG. 2. ABSORPTION SPECTRA OF URANIUM HEXACHLORIDE IN PERFLUOROHEPTANE.

(a) Solubility. Uranium hexachloride dissolves in CCl_4 to give a stable, brown solution. The solubility in CCl_4 and in a number of other solvents has been determined. (Table 27.) Uranium hexachloride appears to react with tetrachlorethylene (UCRL 58) and naphthenic hydrocarbons (Columbia 1). It is slightly soluble in the fluorocarbon C_7F_{16} and in isobutyl bromide.

TABLE 27

SOLUBILITY OF URANIUM HEXACHLORIDE IN VARIOUS SOLVENTS[(a)]

Solvent	Temperature (°C)	g UCl_6/100 g solution
CCl_4	-18	2.64
"	0	4.9
"	20	7.8
6.6% Cl_2-93.4% CCl_4	-20	2.4
12.5% Cl_2-87.5% CCl_4	-20	2.23
"	0	3.98
Liquid chlorine	-33	2.20
Benzene	80	insoluble
CH_3Cl	-24	1.16(b)
Freon 113	45	1.83(b)

(a) (Brown 23)
(b) No apparent reaction between solvent and solute.

(b) Thermal Decomposition. No exact statements are possible at this time on the thermal decomposition of UCl_6. The compound is probably stable up to temperatures of 120°-150°C. The kinetics of the thermal decomposition of UCl_6 have been studied and found to be complicated (UCRL 55). When the rate of decomposition is plotted against time, the curve is found to have a point of inflection; this has been interpreted as indicating a solid phase transition from one crystal form of UCl_6 to another, more stable form. A well defined induction period, decreasing from thirty minutes to five minutes as the temperature is raised from 140° to 170°C, is observed. The induction period may well be a function of the previous history of the sample. The decomposition is also markedly affected by catalysis. Stainless steel and monel metal are active catalysts for thermal decomposition of UCl_6; gold and nickel-plated copper wire are quite inert.

The rate of decomposition of UCl_6 in the vapor phase is negligible by comparison to that in the solid phase. In the range 130°-180°C, the rate constant, k, of the reaction,

$$(89) \qquad 2UCl_6(g) \longrightarrow 2UCl_5(s) + Cl_2(g)$$

is between 10^{-3} and 10^{-1}/min. These wide limits reflect the uncertainty of the vapor pressure data for UCl_6. An activation energy of approximately 40 kcal/mole is required for reaction (89).

(c) Reaction of UCl_6 with Hydrogen Fluoride (Brown 26,27). When UCl_6 is treated with purified, anhydrous liquid hydrogen fluoride at room temperature (in a platinum-lined reactor), UF_5 rather than UF_6

is obtained:

$$2UCl_6 + 10HF \longrightarrow 2UF_5 + 10HCl + Cl_2 \quad (90)$$

(d) Corrosion of Various Substances by UCl_6 (UCRL 70). A number of materials have been examined for resistance of UCl_6. The results are in part contradictory since a number of materials are reported to be inert, whereas kinetic studies indicate that they are powerful catalysts for the decomposition of UCl_6. The discrepancy may arise from the fact that the corrosion tests were performed at 100°C, at which temperature the catalytic effects may not be important. The results of some of these experiments are given in Table 28.

TABLE 28

CORROSION OF METALS BY GASEOUS URANIUM HEXACHLORIDE AT 100°C

Samples	Corrosion	Chlorine Evolution
Au, Monel, Ni	none	none
Nichrome, Ta	v. slight	none
Mo, 18-8 Stainless Steel, C-15 Graphite	none	small amount
German Silver, 85 Spears Graphite	none	large amount
Brass, Pb, Al	slight	small amount from Pb and Brass
Cu, Ag, Hg	severe	?

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TEC-CEW 28	John, G. S., and J. R. VanWazer, CD 3.385.4, Aug. 22, 1945.
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TEC-CEW 30	Sterett, C., I. Halpern, and J. VanWazer, CD-GS-28, Mar. 16, 1945.
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TEC-CEW 32	Young, H. S., "Preparation of Uranium Trichloride by Reduction of the Tetrachloride with Metals," Collected Paper, M.P.T.S., Vol. 11B.

TEC-CEW 33	Miller, A. J., and L. B. Dean, "Preparation of Uranium Tetrachloride with Hexachloropropylene and Other Chlorinated Organic Compounds," Collected Paper, M.P.T.S., Vol. 11B.
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TEC-CEW 35	Young, H. S., and H. F. Grady, "Physical Constants of Uranium Tetrachloride, Collected Paper," M.P.T.S., Vol. 11B.
UCRL 1	Barkelew, C. H., RL 4.6.906, Jan. 18, 1945.
UCRL 2	Altman, D. A., RL 4.6.156, June 11, 1943.
UCRL 3	MacWood, G. E., and D. A. Altman, RL 4.7.600.
UCRL 4	Barkelew, C. H., RL 4.6.929, Aug. 28, 1945.
UCRL 5	Altman, D., RL 4.6.276, Aug. 14, 1945.
UCRL 6	Gregory, N. W., RL 4.6.928, Aug. 24, 1945.
UCRL 7	MacWood, G. E., "Thermodynamic Properties of Some Uranium Compounds," Collected Paper," M.P.T.S., Vol. 11B.
UCRL 8	Altman, D., RL 4.6.166, June 25, 1943.
UCRL 9	Davidson, P., M. Mueller, RL 4.6.250, Feb. 26, 1944.
UCRL 10	Cook, O.H., and R. C. Feber, RL 4.6.926, July 3, 1945.
UCRL 11	Reiber, H., RL 4.6.169, July 3, 1943.
UCRL 12	Reiber, H., RL 4.6.187, July 31, 1943.
UCRL 13	Rosenfeld, S., RL 4.6.58.
UCRL 14	Reiber, H. G., RL 4.7.600, Sec. D, Oct. 24, 1944.
UCRL 15	Polissar, M. J., RL 4.6.35, Nov. 3, 1942; Rosenfeld, S., RL 4.6.52, Mar. 22, 1943.
UCRL 16	Reiber, H. G., and H. A. Young, RL 4.6.54.

UCRL 17	Steele, G., RL 4.6.113, Apr. 13, 1943.
UCRL 18	Reiber, H., RL 4.6.70, Mar. 13, 1943.
UCRL 19	Reiber, H., RL 4.6.105.
UCRL 20	Reiber, H., RL 4.6.67.
UCRL 21	Rosenfeld, S., RL 4.6.119, Aug. 28, 1944.
UCRL 22	Babcock, S. H., RL 4.6.61, July 13, 1943.
UCRL 23	Wood, W. C., H. Bradley, H. S. Carroll, RL 4.6.287, Aug. 1944.
UCRL 24	Kamen, M., RL 4.6.8, Nov. 30, 1942.
UCRL 25	Kinderman, R. L., M. B. Leboeuf, and H. Walter, RL 4.6.99, July 27, 1945.
UCRL 26	Jenkins, F. A., RL 4.6.232, Dec. 15, 1943.
UCRL 27	Dorough, G. D., RL 4.6.283, Aug. 18, 1944.
UCRL 28	Jenkins, F. A., O. E. Anderson, and A. DeHaan, RL 4.6.1.
UCRL 29	Rosenfeld, S., RL 4.6.66, Mar. 23, 1943.
UCRL 30	Schmidt, R., RL 4.6.117, Apr. 24, 1943.
UCRL 31	Gregory, N. W., RL 4.6.923, Aug. 1, 1943.
UCRL 32	Jenkins, F. A., RL 4.6.3.
UCRL 33	Polissar, M. J., RL 4.6.36, Oct. 23, 1942.
UCRL 34	Altman, D., RL 4.6.276.
UCRL 35	Mueller, M., RL 4.6.934, Sept. 18, 1945.
UCRL 36	Reynolds, F. L., and P. H. Davidson, RL 4.6.231, Nov. 30, 1943; RL 4.6.236, Dec. 28, 1943.
UCRL 37	Mueller, M. E., RL 4.6.191, Aug. 19, 1943.
UCRL 38	Booker, J., and A. DeHaan, RL 4.6.6, Nov. 22, 1942.
UCRL 39	Cummings, R., RL 4.6.176, July 27, 1943.
UCRL 40	Davidson, P. H., and I. Streeter, RL 4.6.289, Sept. 5, 1944.

UCRL 41	Cummings, R., and C. Hollingshead, RL 4.6.89, Mar. 26, 1943; RL 4.6.92, Apr. 3, 1943; Cummings, R., RL 4.6.137, May 20, 1943.
UCRL 42	Carter, J. F., F. A. Jenkins, M. Kamen, C. Larson, D. Lipkind, and S. Weissman, RL 4.6.13, Jan. 17, 1943.
UCRL 43	Webb, A. D., RL 4.6.102; RL 4.6.87; Kyle, H. P., RL 4.6.50; Webb, A. D., H. P. Kyle, RL 4.6.51, Mar. 1943.
UCRL 44	Reiber, H. G., RL 4.6.116, Apr. 23, 1943.
UCRL 45	Wilder, C. O., RL 4.6.65, RL 4.6.68, RL 4.6.73, RL 4.6.103, RL 4.6.106, RL 4.6.129, Apr. 26, 1943; Young, H. W., RL 4.6.111, Apr. 20, 1943.
UCRL 46	Mueller, M., RL 4.6.88, Mar. 28, 1943.
UCRL 47	Reynolds, F. L., RL 4.6.80, Feb. 13, 1943.
UCRL 48	Wood, W. C., and H. Bradley, RL 4.6.263, May 20, 1944; Wood, W. C., H. Bradley, and H. S. Carroll, RL 4.6.287, Aug. 29, 1944.
UCRL 49	Wood, W. C., RL 4.7.600, E-1.
UCRL 50	Jenkins, F. A., RL 4.6.97, Apr. 6, 1943.
UCRL 51	Bell, A., RL 4.6.525, Aug. 9, 1943.
UCRL 52	Hubbard, J. V., RL 4.6.168, June 30, 1943.
UCRL 53	Steele, G. D., RL 4.6.99, Mar. 26, 1943.
UCRL 54	Jenkins, F. A., RL 4.6.85A, Feb. 22, 1943; RL 4.6.47, Mar. 9, 1943.
UCRL 55	Altman, D., RL 4.6.161, June 21, 1943.
UCRL 56	Reiber, H., RL 4.6.60.
UCRL 57	MacWood, G. E., RL 4.7.602, Dec. 18, 1945.
UCRL 58	Allen, M. B., RL 4.6.19, Feb. 13, 1943.
UCRL 59	Wood, W. C., and H. Bradley, RL 4.6.288, Sept. 2, 1944.

UCRL 60	Krohm, R., RL 4.6.238, Jan. 4, 1944.
UCRL 61	Davidson, P. H., RL 4.6.86, Mar. 23, 1943.
UCRL 62	Reiber, H. G., RL 4.6.233, Dec. 15, 1943; RL 4.6.125, May 3, 1943.
UCRL 63	Reiber, H. G., RL 4.6.131, May 8, 1943.
UCRL 64	Allen, M. E., RL 4.6.77, Feb. 6, 1943.
UCRL 65	Reynolds, F. L., RL 4.6.78, Feb. 7, 1943.
UCRL 66	Reynolds, F. L., RL 4.6.188, May 2, 1943.
UCRL 67	Davidson, P. H., and J. A. Holmes, RL 4.6.182, July 29, 1943.
UCRL 68	Jenkins, F. A., RL 4.6.47, Mar. 9, 1943.
UCRL 69	Altman, D., D. Lipkin, and S. Weissman, RL 4.6.22, Feb. 27, 1943.
UCRL 70	Lipkin, D., and S. Weissman, RL 4.6.18, Feb. 3, 1943; RL 4.6.112, Apr. 27, 1943; RL 4.5.13, Jan.17, 1943.

CHAPTER XV

BROMIDES, IODIDES AND PSEUDO-HALIDES OF URANIUM

CHAPTER XV

BROMIDES, IODIDES AND PSEUDO-HALIDES OF URANIUM

1. Uranium Tribromide, UBr_3 (MP Ames 1)

Uranium tribromide resembles uranium trichloride in many respects. It is a somewhat more hygroscopic compound, but in a general way undergoes the same reactions and possesses physical properties similar to those of UCl_3. The preparative methods for UBr_3 and UCl_3 are also very similar. The resemblance is emphasized here because the chemistry of UCl_3 is considerably better explored than that of UBr_3, and much qualitative information about UBr_3 may be obtained by analogy from UCl_3.

1.1 Preparation of UBr_3. The oldest method of preparation of UBr_3 is the reduction of UBr_4 with hydrogen (Alibegoff, 1886). This reaction, however, is rather unsatisfactory, and procedures which give a purer product have been developed.

(a) Preparation of UBr_3 from UH_3 + HBr (MP Ames 2-6; MP Chicago 1; UCRL 1). Hydrogen bromide reacts readily and smoothly with uranium hydride at 300°C to form UBr_3:

$$U + 3/2\ H_2 \xrightarrow{250^\circ C} UH_3 \tag{1}$$

$$UH_3 + 3HBr \xrightarrow{300^\circ C} UBr_3 + 3H_2 \tag{2}$$

Suitable apparatus is described in Volume 11B in the Ames paper cited at the head of this section (also see Fig. 1). It is necessary to use pure reagents; traces of oxygen must be removed from the hydrogen, and the bromine used in preparing the hydrogen bromide must be dried over P_2O_5. If uranium metal is available, this is an excellent method of preparation.

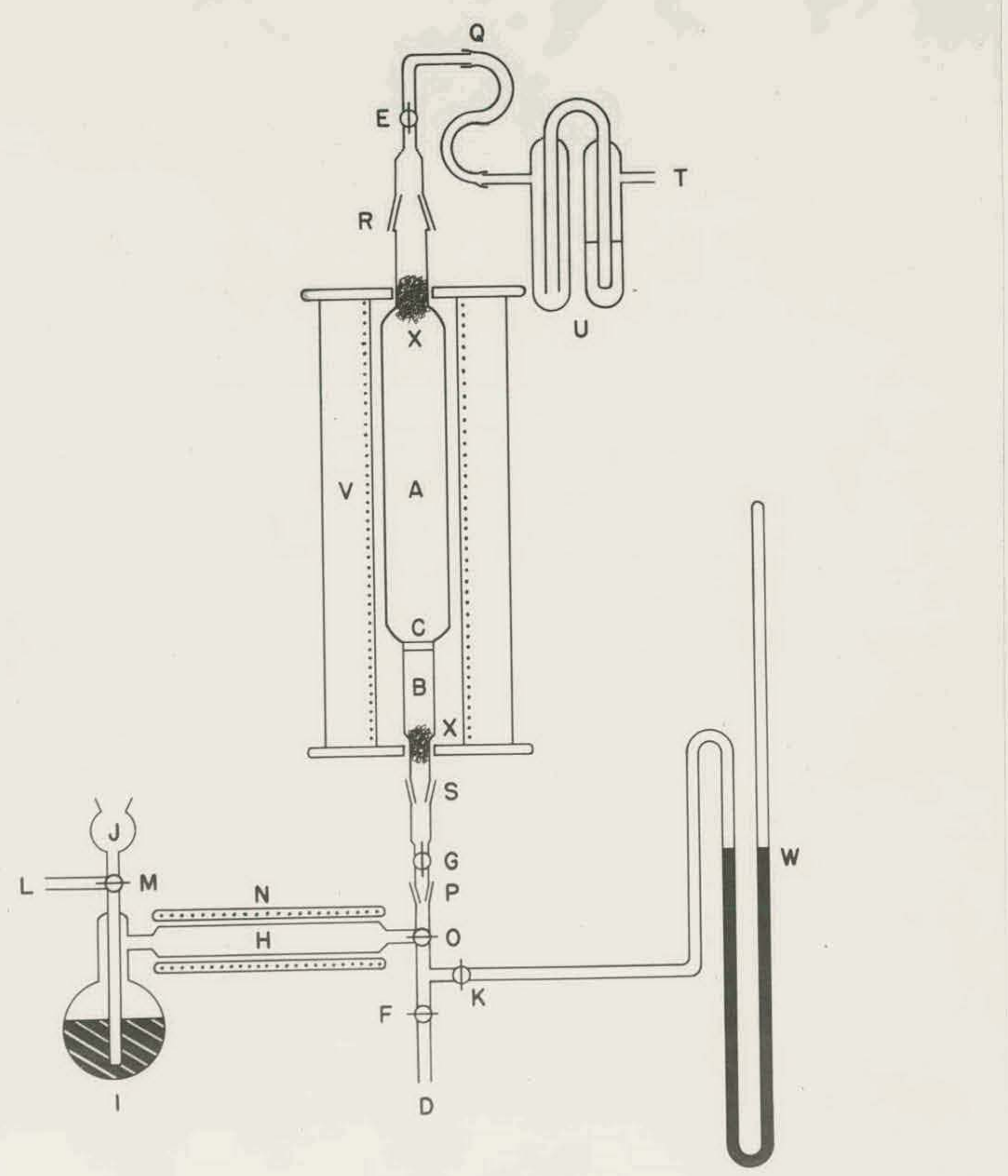


FIG. I. APPARATUS FOR THE PREPARATION OF ANHYDROUS URANIUM TRIBROMIDE

A. REACTION CHAMBER
B. SCRUBBING CHAMBER
C. SINTERED GLASS DISC
D. OUTLET FOR FLUSHING SYSTEM
E. STOPCOCK
F. STOPCOCK
G. STOPCOCK
H. PLATINIZED ASBESTOS
I. BROMINE BUBBLER
J. THISTLE TUBE
K. STOPCOCK
L. GAS INLET
M. THREE WAY STOPCOCK
N. RESISTANCE FURNACE
O. THREE WAY STOPCOCK
P. STANDARD TAPER JOINT
Q. RUBBER TUBING
R. STANDARD TAPER JOINT
S. STANDARD TAPER JOINT
T. OUTLET TO HOOD
U. SULFURIC ACID BUBBLER AND TRAP
V. RESISTANCE FURNACE
W. MANOMETER
X. GLASS WOOL PLUG.

(b) Reaction of Metallic Uranium with Bromine (M P Berkeley 1,2,3). Metallic uranium and bromine vapors react to yield UBr_3:

(3) $$U + 3/2\ Br_2 \longrightarrow UBr_3$$

To obtain UBr_3 stoichiometric quantities are used. A large pyrex tube with a side arm for the bromine is a suitable reaction vessel. The bromine is kept frozen in the reservoir until the metal is heated to 300°-500°C; the bromine is then liquified and the vapors allowed to react with the metal. The uranium may advantageously be powdered by hydride formation and subsequent decomposition. When the bromine is all consumed, the entire system is heated to 500°-550°C. A product analyzed as close to UBr_3 is obtainable in this way.

(c) Reduction of UBr_4 with Hydrogen. Historically the preparation of UBr_3 was first accomplished by hydrogen reduction at temperatures near the melting point of UBr_4 (Alibegoff, 1886; Zimmermann, 1882):

(4) $$UBr_4 + 1/2\ H_2 \rightarrow UBr_3 + HBr$$

It has been found, however, that reduction does not necessarily stop at the tribromide stage and that products with a uranium:bromine ratio significantly less than three are sometimes obtained (MP Ames 6; MP Berkeley 4,5). This observation has been confirmed both by analysis of the product and by measurement of the amount of hydrogen bromide evolved. It is not clear whether reduction to a lower uranium bromide occurs, or whether traces of moisture or oxygen are responsible. The reduction reaction appears to start at 430°C, but the rate is extremely slow below 550°C. At 700°C the rate is rapid, but considerable attack on the quartz reactors is experienced. The uncertainty of the composition of the product, coupled with the fact that the reaction is slow, renders the hydrogen reduction method of doubtful utility.

1.2 Physical Properties of UBr_3. Uranium bromide resembles UCl_3 and the rare earth tribromides, $LaBr_3$ and $NdBr_3$, in its general physical properties. Like these, it is a high-melting, non-volatile crystalline substance.

(a) Melting Point. A number of values for the melting point of UBr_3 are available (MP Ames 7; MP Berkeley 2,6,7; MP Chicago 2; UCRL 1). A value of 755°C found at Ames is not based on a direct determination of the melting point, but is derived from phase rule studies of the U-UBr_3 and UBr_3-UBr_4 systems. At UCRL a value of 730°C was found by direct measurement and is probably more accurate.

(b) Crystal Structure and Density (MP Chicago 3). X-ray methods indicate UBr_3 to have an hexagonal unit cell, with

$$a_1 = 7.926 \pm 0.002\ \mathring{A} \qquad a_3 = 4.432 \pm 0.002\ \mathring{A}.$$

There are two molecules per unit cell, with nine bromine atoms arranged about every uranium atom at an average U-Br distance of 3.12 Å. Uranium tribromide is isomorphous with UCl_3, $LaCl_3$, $NdCl_3$, $LaBr_3$, $PrBr_3$, $La(OH)_3$, and $Nd(OH)_3$ (MP Ames 8,9; MP Chicago 4). The space group is $C6_3/m$ ($C6h^2$).

The density of UBr_3 determined from the x-ray data is 6.53 g/cc. A direct pycnometric determination (in xylene) gave an average value of 5.98 g/cc (MP Ames 10).

(c) Vapor Pressure of UBr_3. The determination of the vapor pressure of UBr_3 has been difficult. The measurements must be made at elevated temperatures where attack on the apparatus is serious. Further, the composition of the residue changes slowly from a uranium: bromine ratio of 1:3 to values approaching 1:2. The ratio in the distillate also varies (from 1:3.2 to 1:3.8), and while an appreciable fraction of the distillate is thought to be UBr_3, some UBr_4 is almost certainly present particularly at temperatures above 900°C. The vapor pressure of UBr_3 has been measured by an effusion method using molybdenum capsules (UCRL 1). The data given in Table 1 are probably the best available for UBr_3.

TABLE 1

VAPOR PRESSURE OF URANIUM TRIBROMIDE (EFFUSION METHOD, Mo CAPSULE)

Temperature (°C)	Vapor Pressure (mm Hg)
600	$2.0x10^{-5}$
650	$1.6x10^{-4}$
700	$1.3x10^{-3}$
750	$8.0x10^{-3}$
800	$3.x210^{-2}$
850	$1.6x10^{-1}$
900	$5.0x10^{-1}$
950	1.6
1000	5.0

The vapor pressure data may be represented by the equation:

$$\log_{10}P_{mm} = \frac{-15,000}{T} + 12.5 \quad (5)$$

This leads to a heat of vaporization of 68 kcal/mole.

A gas saturation (transpiration) method has also been used. (MP Berkeley 1). Tu suppress disproportionation a mixture of UBr_3 and uranium is used. The liquid phase approximated UBr_2 in composition, whereas the distillate corresponded to UBr_3. (Table 2)

TABLE 2

VAPOR PRESSURE OF URANIUM TRIBROMIDE (TRANSPIRATION METHOD)

Temperature (°C)	Vapor Pressure (mm Hg)
915	0.30
1014	1.9
1062	3.1
1124	6.6

The agreement between the two sets of measurements is poor, and it is questionable whether the same phenomenon was being measured. It may be that one or both series of the vapor pressure data actually are the measure of disproportionation rather than of true volatility. Further work is indicated.

(d) Thermochemical Data (UCRL 2). The heat of formation of UBr_3 was determined by measuring its heat of solution in ferric chloride solution. Combination of thermochemical data for other uranium halides with pertinent data from the literature allows the heat and free energy formation of UBr_3 to be computed from this measurement.

(6) $$U_{(c)} + 3/2\ Br_{2(g)} \rightarrow UBr_{3(c)}$$

$$\Delta H_{273} = -181.6 \pm 0.6 \text{ kcal/mole}$$

MacWood (UCRL 3) gives 50.6 e.u. as the value of S_{297} for UBr_3. This leads to the value -49.4 e.u. for the entropy of formation, and -166.9 ± 1.5 for ΔF^{o}_{298}. The origin of these entropy values is obscure and they doubtlessly are based, at least in part, on estimates. No heat capacity data for UBr_3 are available.

No phase transitions have been detected in the temperature range 100°-500°C (UCRL 4).

1.3 Chemical Properties of Uranium Tribromide. Uranium tribromide is a dark-brown, crystalline substance. It is very hygroscopic, much more so than uranium trichloride. At room temperature there is appreciable reaction with the oxygen in air.

(a) Water. Uranium tribromide dissolves in water (with vigorous evolution of gas) to give a clear, dark red-violet solution, which changes its color in 30-60 seconds to the clear, brilliant green characteristic of U(IV) solutions (MP Berkeley 4). The evolved hydrogen has been measured, and the amount corresponds within a few per cent to that calculated for the oxidation from the U(III) to the U(IV) state (MP Berkeley 8).

(b) Other Solvents. (MP Berkeley 4,5,9). Uranium tribromide like UBr_4 is almost insoluble in non-polar solvents. For example, the solubility of UBr_3 in benzene and ethyl bromide is much less than 0.5 g/100 cc of solvent. Anhydrous crystals of UBr_3 undergo no color change in p-xylene. In polar solvents UBr_3 is in general less soluble then UBr_4. Dissolution of UBr_3 in polar solvents usually results in extensive reaction. Thus, in formamide, UBr_3 forms a deep-red solution which in the course of several minutes turns green with the evolution of gas. In formamide-hydrogen bromide (32 g HBr/100 cc formamide) UBr_3 decomposes immediately with vigorous gas evolution to a green solution of U(IV). Addition of UBr_3 to acetamide at 110°-115°C results in the formation of a very deep red solution which in a few seconds turns green with simultaneous gas evolution. In ethanol UBr_3 decomposes rapidly in either the absence or presence of atmospheric oxygen, and hydrogen is evolved. Uranium tribromide is insoluble in inorganic solvents such as PCl_3 and $SnCl_4$ (MP Ames 11).

(c) Reduction of UBr_3. (See (e) below). Calcium metal reduces UBr_3 to metallic uranium in good yield. The customary bomb technique can be used (MP Ames 4, 12; see also Chapter IV). The electrochemical reduction of UBr_3 in molten salt baths has been studied (MP Berkeley 1, 10,11). Solutions of UBr_3 (4 to 10 per cent) in molten $BaBr_2$ at 870°-910°C gave unsatisfactory spongy, non-adherent deposits of uranium metal. However, a 10 to 20 mole per cent solution in $SrBr_2$ at 700°C can be used to deposit uranium on an iron, molybdenum or uranium cathode. The bath operates with about 50 per cent current efficiency. Molten UBr_3 itself is not a satisfactory electrolyte for the deposition of uranium.

(d) Oxidation of UBr_3. The oxidation of UBr_3 to UBr_4 by bromine is discussed in Section 2.3 of this chapter. Oxygen reacts with UBr_3 even at room temperature, but the oxidation products have not been identified. In a qualitative way UBr_3 seems to undergo oxidation more readily than UCl_3.

(e) Disproportionation of UBr_3; Phase Relationships. In connection with the discussion of vapor pressure it was pointed out that the composition of the volatilized material could be interpreted as indicating a partial disproportionation at temperatures above 900°C:

$$2UBr_3 \longrightarrow UBr_2 + UBr_4 \qquad (7)$$

The question of the existence of a divalent halide of uranium naturally aroused interest, particularly after it was observed that metallic uranium could be dissolved in molten UBr_3 to give on cooling solid products with empirical formulae closely approximating UBr_2. The problem was attacked by a phase rule study of the U-UBr_3 system (MP Berkeley 2). The results clearly indicate that no compound is formed in the solution of uranium metal in molten UBr_3. An eutectic is formed when the bromine:uranium ratio lies between 2.85 and 2.9 (corresponding to a mole fraction of UBr_3 of 0.98 to 0.95); cooling results in a mixture of UBr_3 and uranium. These results definitely exclude the existence of a stable compound, UBr_2, at room temperature. The formation of UBr_4 in the vapor pressure studies must therefore find some explanation other than simple dismutation. It seems reasonable to assume a reaction with traces of moisture and oxygen.

The phase diagram for the UBr_3-UBr_4 system has been obtained at Ames (MP Ames 7) (Fig. 2). A simple eutectic system is indicated with negligible solubility in the liquid phase, but appreciable solubility of UBr_3 in solid UBr_4. The eutectic occurs at 76 mole per cent UBr_3 and melts at 490°C.

The systems SrI_2-UBr_3 and $SrBr_2$-UBr_3 have also been studied (MP Berkeley 7). Preliminary indications are that compound formation does not occur in these systems. (Fig. 3)

(f) <u>Complex Compounds; Miscellaneous Reactions.</u> Uranium tribromide undergoes reaction on exposure to ammonia gas. The characteristic brown color of UBr_3 dissappears, and a very bulky green material which has the composition $UBr_3.6NH_3$ forms. Treatment of UBr_3 with liquid ammonia, and drying in vacuum gave a solid which contained between three and four NH_3 groups per UBr_3(MP Berkeley 9).

When UBr_3 is heated in quartz until no further distillate is formed, it is found that the residue is free from bromine. Examination shows it to consist of a water-soluble fraction and a black, insoluble portion,

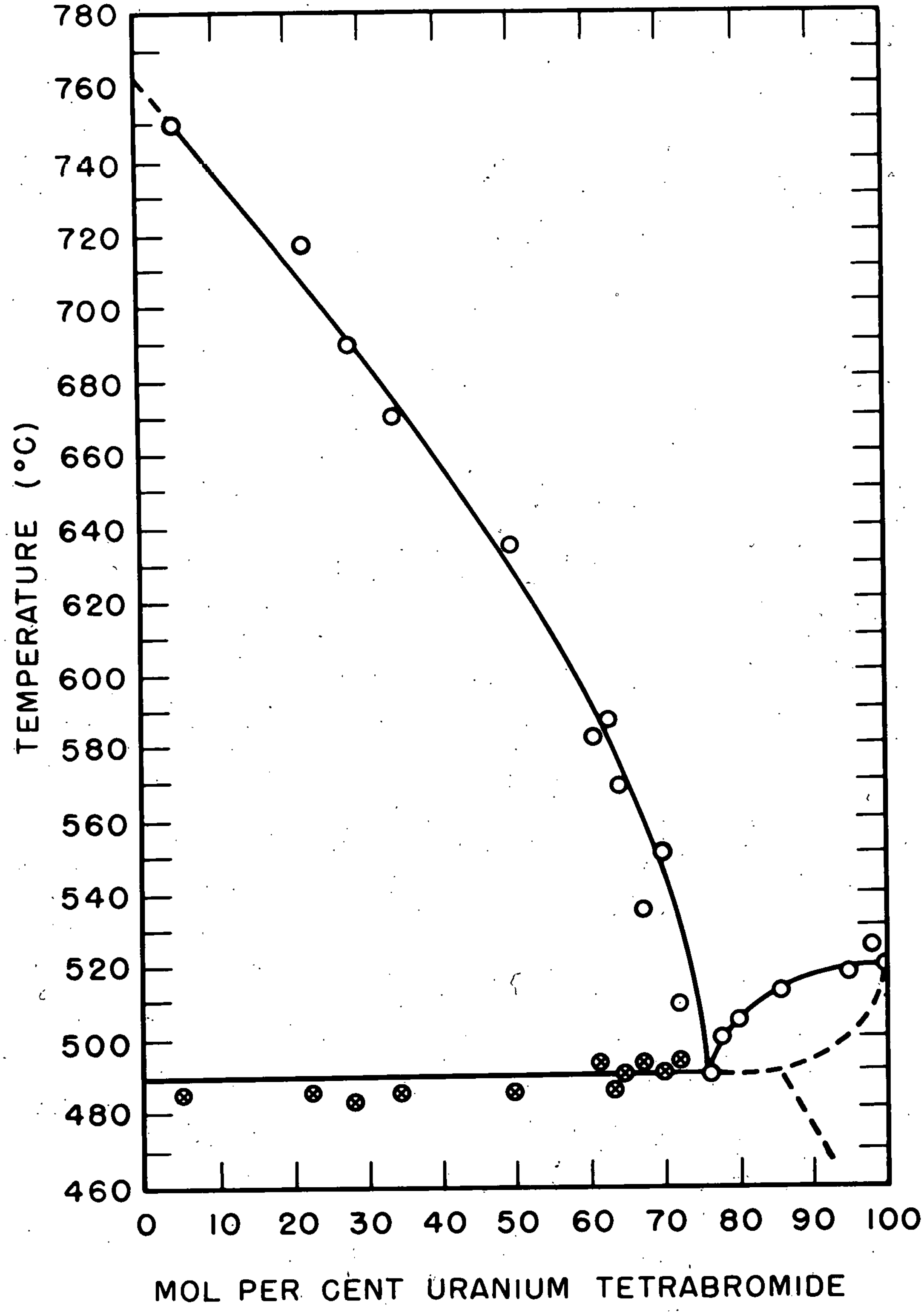
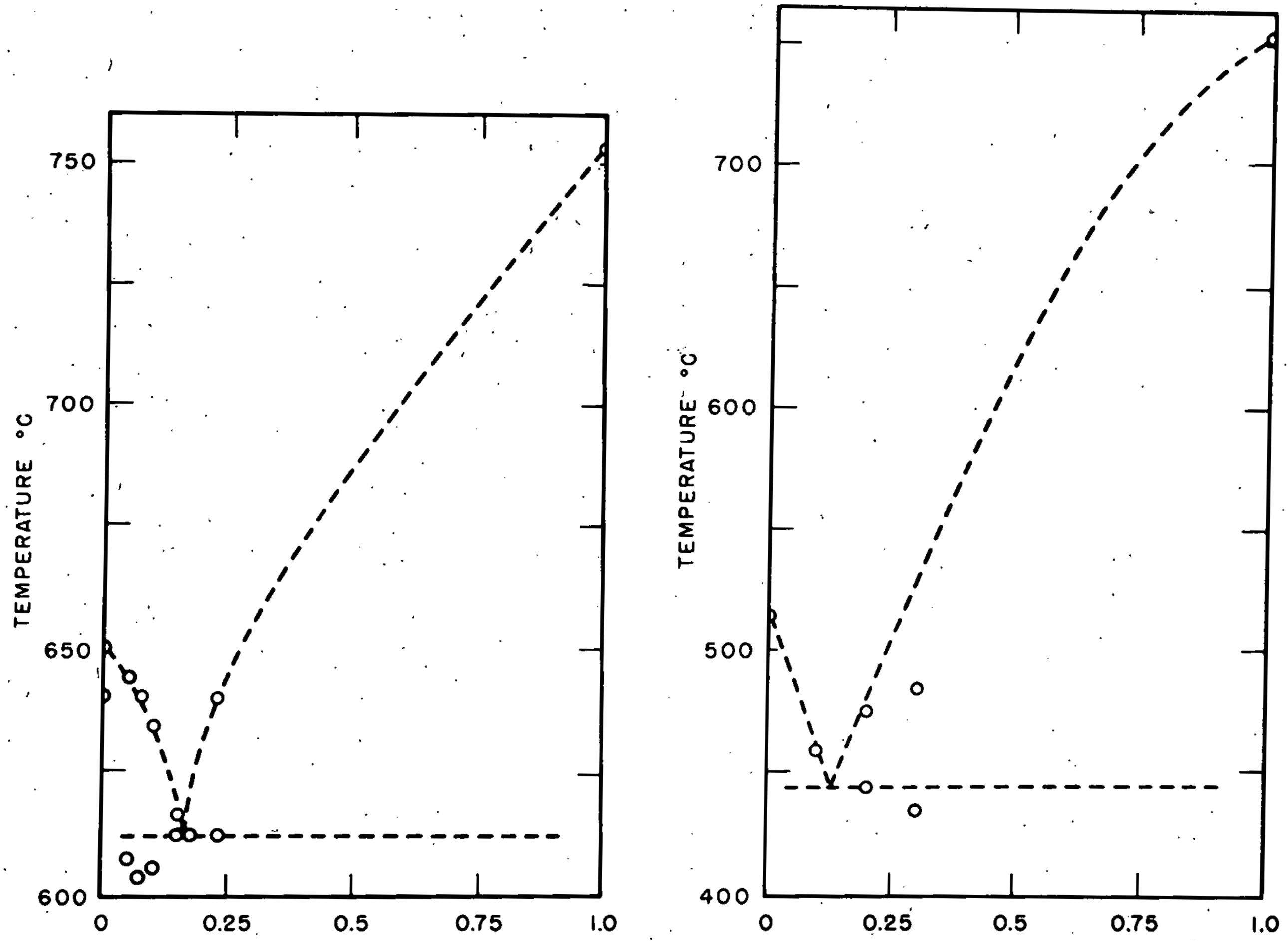


FIG. 2. URANIUM TRIBROMIDE – URANIUM TETRABROMIDE PHASE DIAGRAM.



STRONTIUM BROMIDE –
URANIUM TRIBROMIDE SYSTEM

STRONTIUM IODIDE –
URANIUM TRIBROMIDE SYSTEM

FIG. 3. PHASE DIAGRAMS OF STRONTIUM BROMIDE – URANIUM TRIBROMIDE AND STRONTIUM IODIDE – URANIUM TRIBROMIDE.

The reaction

(8) $12UBr_3 + 2SiO_2 \rightarrow USi_2 + 2UO_2 + 9UBr_4$

has been proposed to explain these observations. Incidentally, this indicates the inadvisability of long-continued heating of UBr_3 in quartz or glass at elevated temperatures. A few metals have been examined for corrosion resistance to UBr_3; molybdenum is found to be quite resistant and is superior to stainless steel (UCRL 1).

2.. Uranium Tetrabromide, UBr_4 (MP Ames 1)

Uranium tetrabromide resembles UCl_4 quite closely in its physical and chemical properties. It is a less stable substance, as evidenced by a smaller free energy of formation:

(9) $U_{(c)} + 2Cl_{2(g)} \rightarrow UCl_{4(c)}$ $\Delta F^{o}_{298} = -229.0 \pm 1.0$ kcal/mole

(10) $U_{(c)} + 2Br_{2(g)} \rightarrow UBr_{4(c)}$ $\Delta F^{o}_{278} = -190.2 \pm 1.5$ kcal/mole

Preparative methods for uranium tetrabromide are less varied than for uranium tetrachloride. The only known reagent which would convert the uranium oxides directly to the tetrabromide is a mixture of carbon and bromine at elevated temperature. Unlike carbon tetrachloride, which is so useful for the preparation of UCl_4, carbon tetrabromide does not come into consideration as a brominating agent, since it completely decomposes at the high temperatures required for reaction. Hydrogen bromide does not convert the uranium oxides at a sufficiently high rate at any temperature despite the fact that the thermodynamic conditions are more favorable for this reaction than for the chlorination of uranium oxides by hydrogen chloride. Since the reaction of oxides with carbon and bromine at elevated temperatures is difficult experimentally, UBr_4 must be prepared from uranium compounds other than the oxides. Free bromine is a sufficiently powerful brominating agent to convert uranium metal and uranium tribromide as well as uranium carbide, nitride or sulfide to UBr_4. Most of these reactions have been studied at Ames.

2.1 <u>Preparation of Uranium Tetrabromide.</u> Since both bromine and UBr_4 are corrosive at elevated temperatures, preparations are usually carried out in glass or quartz. Nickel and gold are fairly resistant, but stainless steel, monel and copper are unsatisfactory (MP Ames 6).

(a) <u>$UO_2 + C + Br_2$.</u> As mentioned above this is the original, but practically inconvenient method for the preparation of UBr_4. It was first employed by Hermann (1861) and followed in principle by all subsequent workers until very recently (Zimmermann, 1882). The efforts of A. Colani (1907) to improve the procedure were unsuccessful. (He also made the claim that hydrogen bromide would convert UCl_4 to UBr_4 at 590°C which is doubtful.) Preparation and purification of UBr_4 by the carbon-bromine reaction were discussed in considerable detail by T. W. Richards (1902) and O. Hönigschmid (1915) who used the purified UBr_4 for atomic weight determinations.

The reaction is carried out by mixing UO_2 or U_3O_8 with excess carbon and treating this mixture with bromine at bright red heat. The bromine is best carried in an inert gas such as nitrogen or CO_2. The UBr_4 condenses in the cooler portions of the apparatus.

(b) <u>Uranium Metal and Bromine (Zimmermann, 1882; MP Ames 13; MP Chicago 5).</u> This reaction is very suitable for the preparation of UBr_4. Bromine (carried in helium gas) acts smoothly with uranium metal turnings at 650°C. The operation is carried out in a quartz apparatus which permits distillation of the product as it forms. The apparatus developed at Ames is shown in Figure 4.

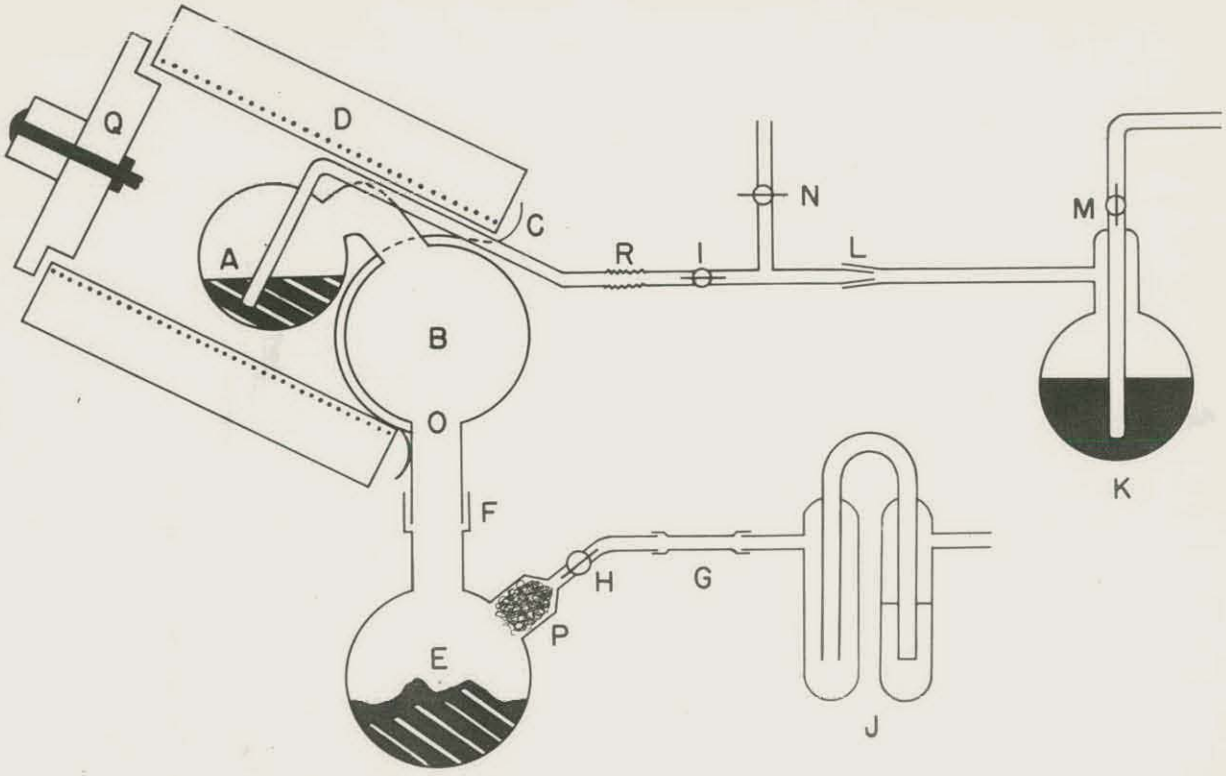


FIG. 4. APPARATUS FOR THE PREPARATION OF ANHYDROUS URANIUM TETRABROMIDE.

A. QUARTZ REACTION FLASK CONTAINING URANIUM TRIBROMIDE OR URANIUM METAL.
B. LITER QUARTZ FLASK USED AS CONDENSING CHAMBER
C. ALUMINUM FOIL REFLECTOR USED FOR INSULATION
D. RESISTANCE FURNACE
E. LITER PYREX FLASK USED AS COLLECTOR
F. QUARTZ TO PYREX JOINT SEALED WITH APIEZON W
G. RUBBER TUBING
H. STOPCOCK
I. STOPCOCK
J. SULFURIC ACID BUBBLER AND TRAP
K. BROMINE RESERVOIR
L. STANDARD TAPER JOINT
M. GAS INLET
N. OUTLET TO HOOD
O. OPENING WHICH OCCASIONALLY PLUGS UP
P. GLASS WOOL PLUG TO RETAIN FINE PRODUCT
Q. REMOVABLE END FOR OBSERVATION
R. QUARTZ TO PYREX SEAL

(c) Uranium Metal and Bromine (By Way of Uranium Hydride) (MP Ames 2). The conversion of uranium metal to the tetrabromide may also be effected by intermediary formation of uranium hydride:

(1) $$U + 3/2\ H_2 \longrightarrow UH_3$$

(11) $$2UH_3 + 7Br_2 \longrightarrow 2UBr_4 + 6HBr$$

This is not as satisfactory as the direct conversion of the metal. The reaction is more difficult to control, and local hot spots are apt to form which eventually clog the apparatus.

(d) Uranium Tribromide and Bromine (MP Ames 2,4,10,14,15,16). This reaction is excellent for preparing UBr_4:

(12) $$2UBr_3 + Br_2 \xrightarrow{300^\circ C} 2UBr_4$$

The bromine is carried by a stream of nitrogen (rigorously purified over copper oxide at 600°C, ascarite, anhydrone and, finally, uranium nitride at 600°C). The reaction proceeds smoothly at 300°C, but the apparatus requires occasional shaking to prevent packing and channeling. Below 200°C reaction is incomplete. The reaction can be carried out without distillation of the UBr_4 which may be advantageous in some cases.

(e) Uranium Nitride and Bromine (MP Ames 17). Essentially, this is a process using uranium metal since the nitride at present can only be prepared from metal. The reaction

(13) $$UN + 2Br_2 \longrightarrow UBr_4 + \tfrac{1}{2}N_2$$

proceeds very smoothly above 600°C. It is convenient to carry the bromine in a stream of purified nitrogen.

(f) Uranium Carbide and Bromine (MP Ames 18-20). The reaction of bromine with uranium carbide provides means for conversion of uranium oxide to tetrabromide:

(14) $UO_2 + 3C \rightarrow UC_2 + CO_2$

(15) $UC_2 + 2Br_2 \rightarrow UBr_4 + 2C$

The reaction of bromine on the carbide is rapid at 800°C. The high temperature required (See $UO_2 + C + Br_2$) is a serious disadvantage because of the difficult corrosion conditions created. Another drawback is that some of the finely-divided carbon produced is carried along by the gas stream and contaminates the product.

(g) Uranium Sulfide and Bromine or Hydrogen Bromide (MP Ames 20, 21). Uranium sulfide is converted by bromine or hydrogen bromide to UBr_4:

(16) $US_2 + 3Br_2 \rightarrow UBr_4 + S_2Br_2$

(17) $US_2 + 4HBr \rightarrow UBr_4 + 2H_2S$

Reaction with bromine occurs at room temperature; hydrogen bromide requires somewhat higher temperatures. The sulfur bromide can be distilled away below 450°C and the reaction is usually completed by distilling the UBr_4 at 600°C. These reactions do not have much practical significance because of the difficulties of obtaining uranium sulfide.

(h) Uranium Dioxide, CS_2, and Bromine ($U_3O_2S_4$ and Br_2)(MP Ames 13, 15,17). It is well known that many oxides (particularly of di- and trivalent metals) are converted to sulfides by treatment with carbon disulfide at elevated temperatures. With uranium oxide the reaction proceeds, however, to give a mixed uranium(IV) oxysulfide (See Chapter 11):

(18) $3UO_2 + 4CS_2 \xrightarrow{900^\circ C} U_3O_2S_4 + 4COS$

When this compound is treated with bromine, reaction occurs at 50°-100°C, and S_2Br_2 forms, which can be removed at 400°C. The residue, a light brown powder, decomposes at 600°C with formation of UBr_4. The residue from this treatment is $UOBr_2$ which in turn decomposes to UO_2 and UBr_4 at 800°C:

(19) $U_3O_2S_4 + 6Br_2 \xrightarrow{50^\circ-100^\circ C} 2UOBr_2 + UBr_4 + 2S_2Br_2$

(20) $2UOBr_2 \xrightarrow{800^\circ-1000^\circ C} UBr_4 + UO_2$

---

(21) $U_3O_2S_4 + 6Br_2 \xrightarrow{800^\circ C} 2UBr_4 + UO_2 + 2S_2Br_2$

If the reaction is completed at 800°C, the net result will be the conversion of three moles of UO_2 to two moles of UBr_4. The residual mole of UO_2 will require reprocessing. This interesting cycle merits further study.

(i) Summary of Preparative Methods. The following table summarizes the reactions discussed above by which uranium tetrabromide can be produced from various uranium compounds and free bromine.

TABLE 3

PREPARATION OF URANIUM TETRABROMIDE

Reaction No.	Reactants (+ Bromine)	Temperature (°C)	Carrier Gas	Products (+ UBr_4)
(22)*	UO_2, C	700-900	N_2, CO_2	CO
(23)	U_3O_8,C	700-900	N_2, CO_2	CO
(10)*	U	650	He	—
(11)	UH_3	?	He	HBr
(12)*	UBr_3	300	N_2	—
(13)	UN	600	N_2	N_2
(15)	UC_2	800	N_2	C
(16)	US_2	450	N_2	S_2Br_2
(21)	$U_3O_2S_4$	800	N_2	UO_2, S_2Br_2

*These reactions are considered most practicable from the point of view of accessibility of starting materials as well as ease of manipulation.

(j) Preparation of UBr_4 from Solution. Since aqueous solutions of UBr_4 may be readily prepared, attempts have been made to prepare anhydrous UBr_4 from them. Solutions of UBr_4 can be made by reducing uranyl bromide electrochemically, or chemically by reducing agents such as uranium metal, or by dissolving hydrated uranium(IV) hydroxide in hydrobromic acid. It has been found that such solutions cannot be dehydrated without very considerable hydrolysis. In this respect aqueous solutions of UBr_4 resemble those of UCl_4 with the difference that hydrolysis occurs even more readily in the case of UBr_4. Hydrolysis can take place even in a stream of hydrogen bromide, which is not surprising when it is recalled that hydrogen bromide is incapable of converting UO_2 to UBr_4. Considerable oxidation occurs when UBr_4 solutions are concentrated under reduced pressure both at room temperature or at 180°C even in an hydrogen bromide atmosphere (MP Ames 22). It has been reported that UBr_4 is formed on photochemical reduction of a solution of UO_3 in alcoholic hydrogen bromide, but this requires verification (Aloy, 1922).

(k) Purification of UBr_4. (MP Ames 6,15,23; Princeton 1) Uranium tetrabromide is best purified by vacuum distillation or sublimation in a stream of inert gas containing a small amount of bromine. Highly purified nitrogen or helium are suitable carrier gases.

2.2 Physical Properties of Uranium Tetrabromide. The physical properties of UBr_4 have not been investigated as systematically as those of UCl_4, and the information available is rather fragmentary.

(a) Melting Point (MP Ames 17,24; UCRL 5). The melting point of UBr_4 has been determined at Ames to be 519 ± 2°C. A value of 516°C was obtained from thermal analysis (UCRL 4).

(b) Boiling Point (MP Ames 17,25). Direct measurement yields a value of 765°C for the boiling point (with decomposition) under 740 mm Hg pressure. Extrapolation from vapor pressure data (transpiration method) gives a value of 761°C at 760 mm Hg which is in satisfactory agreement.

(c) Density. The older values (Richards, 1902) for the density are probably in error. A direct determination, using benzene and xylene as the pycnometer fluids, gave a value of 5.35 g/cc at 26°C (MP Ames 10). There is no x-ray crystallographic data from which the density of UBr_4 can be calculated. The vapor density determined by C. Zimmermann (1882) shows the vapor to exist as a monatomic gas.

(d) Vapor Pressure. The vapor pressure of UBr_4 has been studied by a molecular effusion technique and by a transpiration method. Since different temperature ranges were explored, the results cannot be readily compared except for one point (450°C) where the agreement is satisfactory. The results obtained by the effusion method are given in Table 4.

The results of the vapor pressure determination by the transpiration method are given in Table 5 (MP Ames 1). From these data the following equations have been derived:

(24) For sublimation: $$\log P_{mm} = \frac{-10{,}900}{T} + 14.56$$

(25) For vaporization: $$\log P_{mm} = \frac{-7{,}060}{T} + 9.71$$

$\Delta H_{sublimation}$ = 50,000 cal/mole

$\Delta H_{vaporization}$ = 32,000 cal/mole

ΔH_{fusion} = 18,000 cal/mole

TABLE 4

VAPOR PRESSURE OF URANIUM TETRABROMIDE (EFFUSION METHOD)*

Temperature (°C)	Vapor Pressure (mm Hg)
300	1.08×10^{-4}
330	$8.45, 9.55 \times 10^{-4}$
350	$3.08, 3.24, 3.33 \times 10^{-3}$
365	5.61×10^{-3}
375	1.27×10^{-2}
400	$2.25, 6.23 \times 10^{-2}$
450	2.9×10^{-1}

*(Princeton 1,2).

These data lead to a value of $\Delta H_{\text{sublimation}}$ of 48,700 cal/mole.

TABLE 5

VAPOR PRESSURE OF URANIUM TETRABROMIDE (TRANSPIRATION METHOD)*

Temperature (°C)	Vapor Pressure (mm Hg)
450	0.30
475	0.95
500	2.85
525	9.15
550	13.5
575	24.0
600	40.8
625	70.1

*(MP Ames 17).

Trouton's constant $(\frac{\Delta H}{T})$ is computed to be 31.0 and Hildebrand's constant, 32.8. These values indicated considerable association in the liquid state. The second set of data appear to be more reliable than that obtained by the effusion method; the thermodynamic data based on the transpiration method vapor pressure data is therefore probably more accurate.

(e) Thermochemical Data. The heat of solution of UBr_4 in water has been found to be -33.1 ± 0.1 kcal/mole. By combination with other appropriate data the heat of formation of UBr_4 can be calculated (UCRL 2):

(10) $U_{(c)} + 2Br_{2(g)} \longrightarrow UBr_{4(c)}$ $\Delta H^o_{298} = -211.3 \pm 0.6$ kcal/mole

MacWood (UCRL 5) gives a value of $S_{298} = 58.5$ e.u. for the entropy of UBr_4, from which one can deduce $\Delta S_{298} = -70.8$ and $\Delta F^o_{298} = -190.2 \pm 1.5$ kcal/mole.

The equilibrium constant for the reaction

(26) $UBr_{4(c)} + \frac{1}{2}H_{2(g)} \longrightarrow UBr_{3(c)} + HBr_{(g)}$

has been determined in the temperature range 400°-525°C at the UCRL (5-7). (Table 6). The more recent results of Gregory are probably more precise. Assuming a value of ΔC_p for reaction (26) of -7.59 at 500°C, ΔH_o is found to be 19.913 kcal/mole. The data in Table 6 also leads to $\Delta S_{298} = 23.96$ e.u. for the same equation.

2.3 Chemical Properties of Uranium Tetrabromide. Uranium tetrabromide is a crystalline substance which varies in color from light tan to dark brown, depending on the crystal size. It is very hygroscopic and is rapidly oxidized in moist air to uranyl bromide. Consequently, UBr_4 must be handled in a dry, inert atmosphere.

(a) Solubility (M P Ames 10,26; MP Berkeley 5,9,12). Uranium tetrabromide dissolves readily in water to form a green solution with the

TABLE 6

EQUILIBRIA FOR THE REDUCTION OF URANIUM TETRABROMIDE WITH HYDROGEN

$K = P_{HBr}/P_{H_2}^{1/2}$

Temperature (°C)	Temperature (°K)	$\frac{1}{T} \times 10^3$	K (a)	K (b)
375	648	1.543	0.080	-
400	673	1.485	0.124	0.141
425	698	1.433	0.188	0.170(420°C)
450	723	1.383	0.256	0.250
475	748	1.337	0.365	0.320
500	773	1.294	-	0.440
525	798	1.253	-	0.570

(a) UCRL 7).
(b) UCRL 5).

characteristic properties of U(IV) solutions. The solution is markedly hydrolyzed.

The behavior of UBr_4 in a great number of organic solvents has been studied. Non-polar solvents such as n-heptene, benzene, toluene, p-xylene, bromobenzene, tetralin and carbon tetrachloride neither dissolve uranium tetrabromide nor react with it. Non-polar inorganic liquids such as PCl_3, $POCl_3$, Br_2 and $SnCl_4$ likewise fail to dissolve UBr_4 at temperatures up to 70°C. On the other hand, uranium tetrabromide is soluble in polar solvents. Solvents containing acidic hydrogen, such as acetic acid, methanol, ethanol, phenol and aniline, react with UBr_4 to evolve hydrogen bromide. Polar solvents with oxidizing properties, nitrobenzene, nitromethane or benzaldehyde for example, convert UBr_4 to uranyl bromide. Solvents containing a basic oxygen grouping such as dioxane, acetone, diethyl ether, ethyl acetate and amyl acetate react with UBr_4 to form stable solvates from which UBr_4 cannot be easily regenerated. These latter solutions are green by reflected, and red by transmitted light. Carbonyl containing compounds are much better solvents than those with only an ether linkage. Nitrile such as acetonitrile and benzonitrile dissolve the tetrabromide to the extent of perhaps 5 g UBr_4/100 cc of solvent and form insoluble solvates on standing.

Uranium tetrabromide is insoluble in liquid ammonia but forms insoluble ammoniated salts. Other amines, i.e., aniline, butyl amine, triethyl amine, diethyl aniline and pyridine scarcely dissolve UBr_4 but do form insoluble addition products. Formamide dissolves UBr_4 with the evolution of considerable heat. The formamide solution appears stable at room temperature, but at temperatures above 100°C some reaction occurs as evidenced by the formation of a precipitate. Uranium tetrabromide is very soluble in molten acetamide (50 g UBr_4/100 cc acetamide). The solution appears to be perfectly stable at 145°C for several days, and is identical in color and absorption spectrum with the formamide solution. Some quantitative data on the solubility of UBr_4 in various solvents are summarized in Tables 7 and 8.

The solubility of UBr_4 in some molten salts has also been determined. At 900°C a ten per cent UBr_4 solution in $BaBr_2$ can be prepared. Uranium tetrabromide is also soluble to an unknown extent in a molten NaCl-KCl mixture at 725°C (MP Berkeley 10).

(b) <u>Oxidation Reactions</u>. Oxygen converts UBr_4 to UO_2Br_2. Chlorine converts UBr_4 to UCl_4. Bromine (liquid) does not react with UBr_4 even at 230°C (Zimmermann, 1882). No evidence for the formation of UBr_5 or higher bromides is found when UBr_4 is distilled with bromine vapor at 750°C.

TABLE 7

SOLUBILITY OF URANIUM TETRABROMIDE IN ORGANIC SOLVENTS AT 25°C [(a)]

Solvent	Density of Saturated Solution (g/cc)	g UBr_4/100 g Solvent (by U analysis)
Acetic acid	1.573	64.81
Methyl alcohol	1.841	185.2
Ethyl acetate	1.523	91.3
Amyl acetate	1.126	35.3
Dioxane	1.057	2.84
Nitrobenzene	----	17.86
Nitromethane	1.271	14.5
Benzene [(b)]	0.869	0.0
Carbon tetrachloride	1.583	0.0
n-Heptane	0.678	0.0

(a) MP Ames 26)
(b) UBr_4 is also insoluble in toluene, p-xylene and tetralin.

(c) Reduction Reactions. Hydrogen reduces UBr_4 to UBr_3 at 470°-700°C.

(26) $$UBr_4 + \tfrac{1}{2}H_2 \longrightarrow UBr_3 + HBr$$

The evolution of HBr falls sharply when reduction to the UBr_3 stage is achieved (MP Berkeley 5). (See preparation of UBr_3, Sec. 1.1).

Calcium and magnesium reduce UBr_4 to uranium metal. Owing to the volatility of UBr_4, a pressure bomb is required for the reaction. Uranium tetrabromide can be reduced to metal electrochemically or from molten salt solution (MP Berkeley 10), or from solutions of UBr_4 in certain organic solvents (MP Berkeley 5,9,12). Extensive, albeit inconclusive,

TABLE 8

SOLUBILITY OF URANIUM TETRABROMIDE IN VARIOUS SOLVENTS [a]

Solvent[b]	Solubility (g UBr_4/100 cc Solvent)	Color
Ethyl Bromide[c]	v. sl. sol.	Highly colored
Ethyl Bromide (SO_2)[c]	v. sl. sol.	Highly colored
Bromobenzene	v. sl. sol.	Highly colored
Diethyl ether	sl. sol.	Reddish-orange
Dioxane	sl. sol.	Reddish-orange
Acetone	15	Dark red-brown
Acetone (SO_2)	30	Dark red-brown
Acetic acid	55	Dark red-brown
Nitrobenzene	3	Dark violet-red
Formamide	55	v. dark green
Formamide (HBr)	5	Dark red-brown

(a) (MP Berkeley 12).
(b) (SO_2) indicates the solvent to be saturated with SO_2 and (HBr) indicates the presence of about 40 g HBr/100 cc formamide.
(c Five per cent benzene by volume added.

investigations have been carried out at Berkeley on this subject. Solutions of UBr_4 in benzene, ethyl bromide, bromobenzene, diethyl ether, dioxane, acetone, acetic acid and nitrobenzene give complex, non-metallic deposits at the cathode. Acetonitrile, benzonitrile, water and liquid ammonia solutions also fail to give metal. From solutions in formamide, acetamide and ethyl alcohol, however, deposits are obtained (on platinum cathodes) which have been claimed to be metallic uranium. The identification of the deposit was made on the basis of its insolubility in water and solubility in dilute hydrochloric acid with evolution of gas. Unfortunately, certain uranium compounds other than the metal may behave in this way, and consequently the identity of the deposit remains in doubt. The efficiency of the electrolysis is very low (about five per cent) even under the most favorable conditions attained. These procedures, therefore, have little or no practical significance. Nevertheless further studies on the complex phenomena associated with the electrolytic behavior of these organic solutions may be of interest.

(d) Thermal Decomposition of UBr_4. Distillation of UBr_4 in a stream of nitrogen leads to partial decomposition (Hönigschmid, 1915):

(27) $$UBr_4 \longrightarrow UBr_3 + \tfrac{1}{2}Br_2$$

Uranium tetrabromide vapor is reduced to metallic uranium on a hot filament in an evacuated tube. (See Production of Metallic Uranium by Thermal Decomposition, Chapter IV.)

(e) Coordination Compounds. Uranium tetrabromide absorbs ammonia gas at room temperature and atmospheric pressure with slight evolution of heat. Treatment of UBr_4 for one hour followed by pumping for five minutes gives a grey solid, $UBr_4.4NH_3$. Liquid ammonia gives solids varying in composition from $UBr_3.5NH_3$ to $UBr_4.6NH_3$. The hexa-ammoniate is white with a greenish tinge (MP Berkeley 9).

It has been reported (Aloy, 1899) that UBr_4 vapor reacts with alkali metal bromides at elevated temperatures to give double salts of the type M_2UBr_6. The reaction is performed in the same way as with the corresponding chlorine compound, but is more difficult. The product obtained from KBr and UBr_4 vapor is a green substance, easily soluble in water. A similar sodium compound has also been prepared. Data relating to these compounds are meager and their existence and composition require verification.

(f) Corrosion (MP Ames 6; Princeton 3). The behavior of a number of metals and alloys in molten UBr_4 has been studied to find satisfactory materials for handling UBr_4 in addition to quartz or glass. At 775°C nickel and chromel A appear to be the most inert toward molten UBr_4 of the metals studied. Stainless steel disintegrates completely but platinum appears quite resistant. Gold-plate appears to be quite resistant and more satisfactory than platinum plated metals.

3. Uranium (III) and (IV) Iodides, UI_3 and UI_4

Uranium tri- and tetraiodide are best discussed together because of their ready interconversion. The tetraiodide differs from the other U(IV) halides in being thermally unstable. We recall that uranium tetrachloride is not decomposed to UCl_3 at any conveniently attainable temperature (at atmospheric pressure), while uranium tetrabromide undergoes only slight decomposition to tribromide at temperatures of the order of 700-800°C. Uranium tetraiodide, on the other hand, so readily decomposes to UI_3, and I_2 that even at comparatively low temperatures, it is necessary to specify the partial pressure of iodine in the system

$$UI_4 \rightleftharpoons UI_3 + \tfrac{1}{2}I_2 \tag{28}$$

in order to know which of the uranium iodides will be stable.

The only uranium iodide mentioned in the older literature was UI_4 (Gmelin, 1936). Guichard (1907), in an investigation based on an observation of Moissan (1896), treated uranium metal at 550°C.

in a sealed tube with iodine vapor at one atmosphere pressure and obtained a product whose analysis showed it to be UI_4. However, Guichard described this compound as melting above 500°C and being practically non-volatile, which are characteristics of UI_3 rather than UI_4.

Uranium carbide appears to react with iodide, but it has not been possible to obtain pure products this way (MP Ames 27); however, more recent results (UCRL 8) make it likely that this is a potentially useful reaction.

Early attempts to prepare uranium tetraiodide by the action of iodine on a mixture of uranium dioxide and carbon failed (Hermann, 1861). An examination of the pertinent thermodynamic data indicates that the equilibrium of this reaction is unfavorable for iodination. Attempts to prepare uranium iodides by iodination of UO_2 with AlI_3, SbI_3 or BiI_3 have not hitherto been successful, despite the fact that a reaction is known to occur with these compounds (UCRL 8). Some UI_4 is apparently produced when uranium tetrachloride is treated with hydrogen iodide, but the product is heavily contaminated with chlorides (Colani, 1907). Preparations in aqueous solution have also been investigated. It was found that aqueous solutions of uranium iodide can be prepared by dissolving hydrated U(IV)-hydroxide in hydroiodic acid. Attempts to dehydrate this solution were unsuccessful: products containing considerable amounts of free iodine were obtained after the removal of the solvent (Sendtner, 1879). Recently, this work was repeated at the Metallurgical Laboratory (MP Chicago 6,7). The dehydration was effected either in vacuum or in a stream of hydrogen and hydrogen iodide, and the products analyzed between U:I = 2.70 to 2.73. In view of the diffi-

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culties experienced in dehydrating solutions of the other U(IV) halides (cf p.), it is not surprising that compounds of such low iodine content---presumably containing oxide---were obtained.

3.1 Preparation of UI_3 and UI_4 by Reaction of Uranium with Iodine. The most satisfactory method for the preparation of both iodides remains the direct combination of the elements. For the preparation of UI_3, the stoichiometric quantity of iodine is slowly distilled into an evacuated flask containing finely divided uranium at 350°C. When all of the iodine has been absorbed, the reaction vessel is sealed off and heated, first at 130°C for several hours, and then at 570°C for 15 to 20 hours. The product is practically pure UI_3 with very little UI_4 (MP Berkeley 11). The same procedure may be used to prepare UI_4, but in this case it is well to attach to the system an iodine reservoir so that the partial pressure of iodine may be maintained close to one atmosphere during the entire course of the reaction.

The reaction may also be carried out in a flow system, which is preferable when large quantities are to be prepared. Figure 5 shows the apparatus used at UCRL. A horizontal reactor is employed which is connected to a vacuum line. A reservoir of iodine is attached to the reactor inlet, and iodine vapor is pumped through metallic uranium heated to 525°C. The collector is separated from the reactor by a sintered glass disc and is maintained at 400°C. The desired partial pressure of the iodine is obtained by immersion of the iodine reservoir in a bath of 30°C. The reaction is slow, but good conversion yield is obtained and the product is 98-99 per cent pure UI_3 (UCRL 8).

To prepare UI_4 the same system may be employed. The only differ-

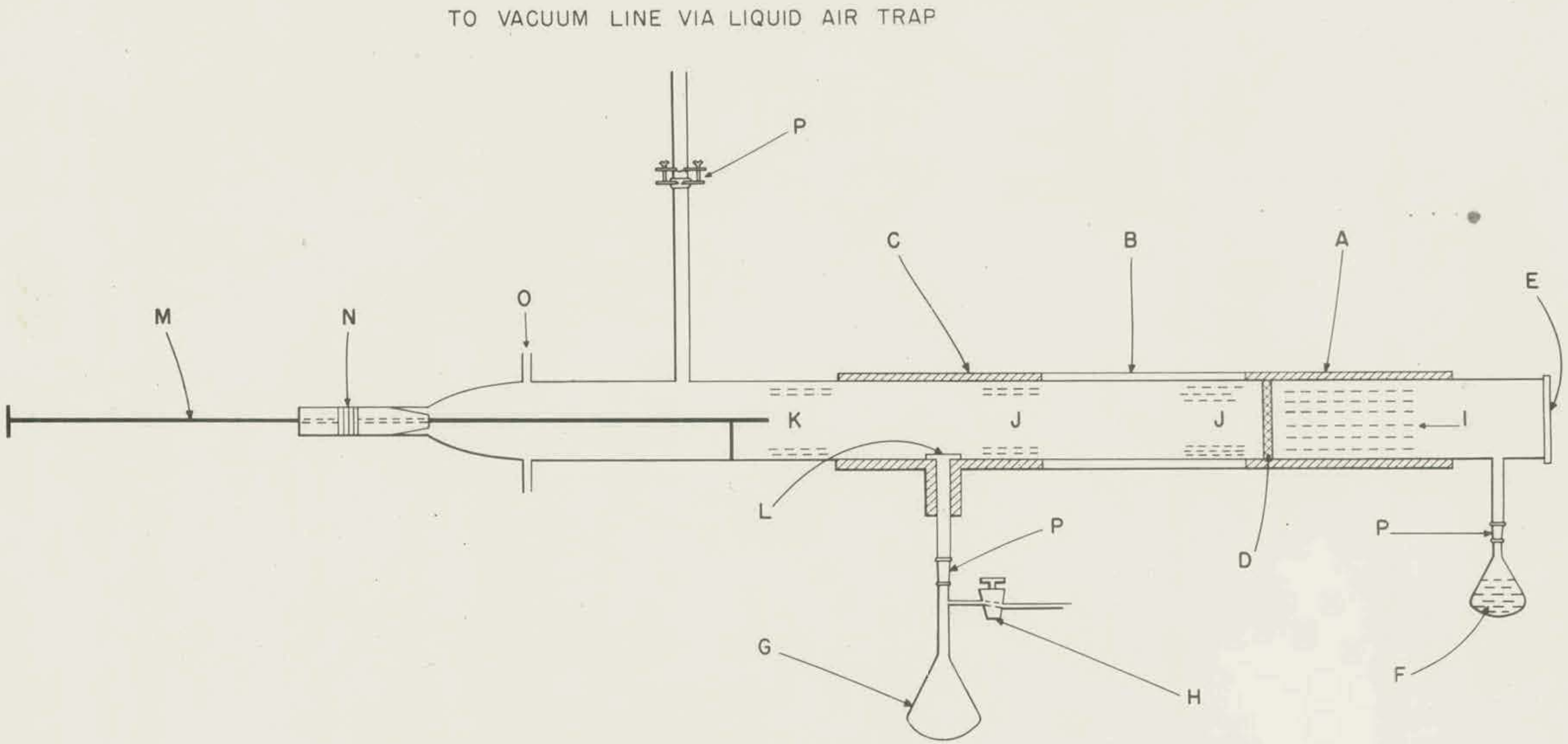

FIG. 5. APPARATUS FOR THE PREPARATION OF URANIUM TRIIODIDE

A. FURNACE – REACTION ZONE – 525°C
B. FURNACE – CONDENSATION – 400°C
C. FURNACE – CONDENSATION – 350°C
} EACH UNIT APPROX. 10" LONG
D. PERFORATED ALUNDUM DISC
E. GROUND GLASS SEAL (SEALING WAX)
F. IODINE
G. URANIUM TRIIODIDE COLLECTOR
H. STOPCOCK FOR EVACUATION OF COLLECTOR AFTER REMOVAL FROM TUBE
I. URANIUM METAL CHARGE – INTRODUCED AT (E)
J. POSITION OF MAXIMUM URANIUM TRIIODIDE DEPOSITION
K. LOCATION OF URANIUM TETRAIODIDE DEPOSITION
L. COVER PREVENTING CONTAMINATION OF COLLECTOR
M. STAINLESS STEEL RAKE FOR TRANSFER OF URANIUM TRIIODIDE DEPOSIT
N. WILSON SEAL ATTACHED TO SYLPHON BELLOWS
O. GROUND GLASS SEAL (SEALING WAX)
P. GROUND GLASS JOINTS

ence is that the partial pressure of iodine must be high enough to prevent the equilibrium

$$UI_4 \rightleftharpoons UI_3 + \tfrac{1}{2}I_2 \qquad (28)$$

from being displaced to the right. A pressure of 100-200 mm Hg (i.e. an iodine reservoir temperature of 120°-140°C) is adequate for this purpose. To prevent the iodine from being pumped through the system too rapidly, connection to the vacuum line is made through a capillary tubing. The proper temperature of the collector is 300°C. The iodine pressure in the system must not be allowed to drop until the collector tube is cold.

In preliminary work on this method of preparation, the products obtained when iodine was passed over uranium metal at 500°-530°C were deposited on collectors possessing a thermal gradient. The collector was then cut into sections and the composition of the sublimate determined as a function of the temperature of the surface (UCRL 9). (Table 9)

TABLE 9

IODINE: URANIUM RATIO AS A FUNCTION OF CONDENSATION TEMPERATURE

Temperature (°C) Range	Iodine: Uranium Ratio
310-386	3.05-2.99
278-354	3.65-3.19
290-250	4.54-4.20
235-253	5.69

The results indicate the optimum condensation ranges for UI_3 and UI_4, and also provide evidence for the existence of a higher iodide. Further investigation of this point would be valuable.

A satisfactory procedure for UI_4 preparation is iodination of UI_3. A vertical reactor is used, with liquid iodine in the bottom and UI_3 in a constricted tube above. The UI_4 formed melts and falls into the pool of excess iodine.

Another iodination reaction which has been investigated is that of uranium hydride with methyl iodide at 275°-300°C. The reaction is rapid and yields UI_3, but no information on the purity of the product is available (MP Ames 28).

3.2. Physical Properties of UI_3 and UI_4. The absence of reliable data on the physical properties of the iodides is a serious gap in our present knowledge of uranium halide chemistry.

(a) Melting and Boiling Points (MP Berkeley 13). The melting point of UI_3 has been estimated as 680°C. The melting point of UI_4 is 506°C (measured in an atmosphere of iodine); its boiling point was estimated as 762°C.

(b) Crystal Structure (MP Chicago 8). Uranium triiodide and uranium tetraiodide are both black, needle-like crystalline substances. Uranium triiodide is ortho-rhombic with four molecules per unit cell:

$$a_1 = 13.98 \pm 0.02\ \text{Å}, \quad a_2 = 4.33 \pm 0.02\ \text{Å}, \quad a_3 = 9.99 \pm 0.02\ \text{Å}$$

The calculated density is 6.76 g/cc. The substance is isomorphous with LaI_3, $NdBr_3$, and $SmBr_3$, and the space group is Ccmm (D_{2h}^{17}). The atomic positions are:

$4\ U$ in $\pm(X_1\ 0\ \tfrac{1}{4})$ with $X_1 = 0.250$

$4\ I$ in $\pm(X_2\ 0\ \tfrac{1}{4})$ with $X_2 = 0.069$

$8\ I$ in $\pm(X_3\ 0\ Z_3)$ with $X_3 = 0.361$, $Z_3 = -0.050$

Each uranium atom is bonded to eight iodine atoms, with an average interatomic distance, U - I = 3.35 Å.

There are no crystallographic data available for UI_4.

(c) <u>Vapor Pressure of UI_4</u> (Princeton 1). Uranium triiodide is relatively nonvolatile, thereby resembling UCl_3. Uranium tetraiodide is more volatile and a number of determinations of its vapor pressure have been made. These measurements are complicated by the dissociation of UI_4 to UI_3 and iodine, and consequently it is difficult to assess the precision of the results. As a rough indication of the volatility of UI_4, the data are probably satisfactory. (Table 10)

TABLE 10

VAPOR PRESSURE OF URANIUM TETRAIODIDE (EFFUSION METHOD)

Temperature (°C)	Vapor Pressure (mm Hg)
300	2.4×10^{-5}
330	2.32×10^{-4}
350	9.48×10^{-4}
360	1.98×10^{-3}
380	7.04×10^{-3}
410	4.25×10^{-2}

The heat of sublimation of UI_4 is then ΔH_s = 52,800 cal/mole, a value which seems high in comparison with those found for other U(IV) halides. More recent work at UCRL confirmed these values roughly; the vapor pressure data found there could be represented by the following equation (cf. MP Ames 28; UCRL 10):

$$\log p = 15.53 - \frac{11.52 \times 10^3}{T} \tag{29}$$

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(c) *Thermochemical Data* (UCRL 3). The following heats and free energy of formation of UI_3 and UI_4 have been determined at the UCRL:

(30) $$U_{(s)} + 3/2\ I_{2(g)} \longrightarrow UI_{3(s)}, \quad \Delta H_{298} = -136.9 \pm 0.6 \text{ kcal/mole}$$

(31) $$U_{(s)} + 2I_{2(g)} \longrightarrow UI_{4(s)}, \quad \Delta H_{298} = -156.7 \pm 0.6 \text{ kcal/mole}$$

The entropies of $UI_{3(s)}$ and UI have been estimated to be S_{298} = 59.5 e.u. (UI_3) and S_{298} = 68.0 e.u. (UI_4). This gives for the free energies: $\Delta F^{\circ}_{298} = -123.2 \pm 1.5$ kcal/mole for UI_3 and $\Delta F^{\circ}_{298} = -136.2 \pm 1.5$ kcal/mole for UI_4.

3.3. Chemical Properties of UI_3 and UI_4.

Uranium Iodides and Water. The uranium iodides are very hygroscopic and dissolve readily in water. Uranium triiodide forms a beautiful dark-red solution; UI_4 solutions have the characteristic green color of the U(IV) ion (UCRL 9). Solutions of UI_4 in water are extensively hydrolyzed as indicated by their strong acid reaction.

The dissolution of UI_3 in water often is accompanied by reaction. Freshly prepared the substance reacts quite violently with water (or even moist air) giving dense clouds of iodine. Preliminary heating to 800°C greatly moderates these reactions (MP Ames 28).

Reduction of Iodides. Hydrogen reduces UI_4 at moderately elevated temperatures to UI_3 and HI. Reduction of UI_3 may be effected electrochemically, metallic uranium being produced by electrolysis of a solution of UI_3 in molten SrI_2 (MP Berkeley 11). A tungsten anode and molybdenum cathode can be used; the bath is maintained at 540°C.

Oxidation of Iodides. Uranium triiodide is moderately stable in acid, oxygen-free solutions, but is rapidly oxidized in alkaline solution

(MP Chicago 9,10). Chlorine reacts with UI_4 at room temperature with evolution of heat. Oxygen or dry air converts UI_3 and UI_4 to U_3O_8 at elevated temperatures and to UO_2I_2 at room temperature. Formation of intermediates such as UOI_2 has been suspected in the latter reaction but no definite results are available (MP Chicago 6).

Thermal Decomposition of UI_4. As mentioned before (cf. equation 28) an equilibrium exists between UI_3, UI_4 and I_2. The dissociation pressures of iodine in equilibrium with solid UI_3 and UI_4 have been measured (UCRL 11). (Table 11)

TABLE 11

DISSOCIATION PRESSURE OF IODINE IN EQUILIBRIUM

WITH URANIUM TRIIODIDE AND URANIUM TETRAIODIDE

Temperature (°K)	Iodine Pressure (mm Hg)
523	8.82×10^{-8}
588	3.82×10^{-6}
625	1.84×10^{-5}
644.2	4.17×10^{-5}
666	8.05×10^{-5}

Assuming a value of $\Delta C_p = -1.54$ for equation (28), the following relationships can be calculated (UCRL 3):

$$\Delta H = 18{,}720 - 1.54\ T$$

$$\Delta H_{298} = 18.3 \text{ kcal/mole}; \quad \Delta F^{\circ}_{298} = 11.51 \text{ kcal/mole};$$

$$\Delta S_{298} = 22.64 \text{ e.u.}$$

These data may be used to calculate the partial pressure of iodine required to prepare either UI_3 or UI_4 by the reaction of uranium and iodine.

The thermal decomposition of uranium tetraiodide finds practical application in the "hot-wire" method for preparing uranium metal (UCRL 12). The process depends on the thermal dissociation of UI_4 at sufficiently high temperatures:

$$UI_{4(g)} \longrightarrow U_{(c)} + 2I_{2(g)} \qquad (31)$$

The decomposition is accomplished by means of an incandescent filament in an evacuated system. Uranium tetraiodide is thermodynamically unstable with respect to its elements at temperatures over 1300°K. A difficulty is introduced by the decomposition of UI_4 to I_2 and the non-volatile UI_3 (according to equation 28). The amount of gaseous iodine present must be very carefully controlled to achieve a favorable relation between the desired reaction (31) and the undesirable reaction (28). These two decomposition equilibria have therefore been studied in some detail (cf. Chapter IV, "Preparation of Metallic Uranium" p.)

Miscellaneous Reactions. At elevated temperatures, UI_3 is a rather corrosive substance; glass or porcelain are attacked with the formation of silicon at 800°C. Of the metals, nickel and silver are more resistant than platinum (MP Ames 28).

4. Uranium (III) and (IV) Mixed Halides (UCRL 13) (MP Ames 29)

The crystal structures of the tri- and tetravalent uranium halides are such that in any particular compound it is possible to replace some of the halogen atoms by others over a wide range of compositions. For certain stoichiometric proportions the solid solutions possess maximum stability and behave like true compounds. Six classes containing eighteen individual compounds of the type UX_nY_{4-n} (X and Y being two different halogens) can exist. At least one compound of each class has been prepared; a number of trivalent mixed halides are also known.

The methods of preparation of these compounds can not be based on displacement of one halogen atom by another, since such reactions fail to occur. The two methods for the preparation of U(IV) mixed halides are (a) the treatment of a trivalent uranium halide with an halogen of higher atomic number, and (b) the reaction of two different tetrahalides at high temperatures. The mixed U(III) halides can be prepared (a) by thermal decomposition of mixed U(IV) halides, (b) by hydrogen reduction of mixed U(IV) compound, and (c) by fusion of two trivalent halides.

Table 12 lists all of the mixed halides known at present. Their preparation and most of their properties will be discussed individually in the order in which the compounds appear in the table; but, for the sake of convenience the vapor pressures and thermochemical data of all mixed halides will be presented together in review form in sections 4.6 and 4.7.

The most extensive research in this field has been carried out at the Radiation Laboratory of the University of California. For details the papers by Gregory in Volume 11 B should be consulted.

4.1. Uranium(IV) Chloro-, Bromo- and Iodofluorides.

(a) Uranium Monochlorotrifluoride, $UClF_3$ (MP Ames 30, 31). This compound has been prepared by the reaction:

(32) $$UF_3 + \tfrac{1}{2}Cl_2 \longrightarrow UClF_3$$

TABLE 12

URANIUM(III) AND (IV) MIXED HALIDES

Compound	Method of Preparation	M.P.* (°C)	B.P. (°C)	Stability	Temperature at which v.p.=10^{-3}mm* (°C)	$\triangle F^{\circ}_{298}$ (kcal/mole)	$\triangle H_{298}$ (kcal/mole)	$\triangle S_{298}$ (e.u.)
$UClF_3$	$UF_3 + \frac{1}{2}Cl_2$			Stable, but cannot be volatilized				
UCl_2F_2	$UO_2F_2 + CCl_4$	(460)		Disproportionates to UCl_4 and UF_4				
$UBrF_3$	$UF + \frac{1}{2}Br_2$			Stable to 450 C				
UIF_3	$UF_4 + I_2$			Stable below 100°C				
$UBrCl_3$	$UCl_3 + \frac{1}{2}Br_2$	521	784	Sublimes without decomp.	356	-220.3 ± 1.5	-241.6	50.0
UBr_2Cl_2	$UCl_4 + UBr_4$	510	780	Sublimes without decomp.	340	-210.5 ± 1.5	-230.6	57.7
UBr_3Cl	$UCl_4 + 3UBr_4$	502	771	Sublimes without decomp.	341	-200.5 ± 1.5	-220.1	60.7
$UICl_3$	$UCl_3 + \frac{1}{2}I_2$	<490		Evolves I_2 above 250°C	(340)	-206.4 ± 1.5	-227.3	53.1
UI_2Cl_2	$UI_4 + UCl_4$	<500		Evolves I_2 above 250°C	(340)			
UI_3Cl	$3UI_4 + UCl_4$	<500		Sublimes without decomp. at low I_2 pressure in system	(340)			
UI_3Br	$3UI_4 + UBr_4$	< 500	-	Evolves I_2 at 250°C. Less stable than UI_3Cl	(330)			
UI_2Br_2	$UI_4 + UBr_4$	< 500		Evolves I_2 at 300°C	(330)			
$UIBr_3$	$UBr_3 + \frac{1}{2}I_2$	478		Sublimes without decomp. at low I_2 pressure in system	330	-177.5 ± 1.5	-195.4	70.9

* Figures in parentheses are estimated values.

TABLE 12
(continued)

Compound	Method of Preparation	M.P. (°C)	B.P. (°C)	Stability	Temperature at which v.p.=10^{-3}mm* (°C)	ΔF^{o}_{298} (kcal/mole)	ΔH_{298} (kcal/mole)	ΔS_{298} (e.u.
$UBrCl_2$	$2UCl_3 + UBr_3$	(800)		Stable	(700)	-187.2 ± 1.5	-202.1	44.6
UBr_2Cl	$UBr_3Cl + H_2$	(775)		Stable	(700)	-178.0 ± 1.5	-191.9	[illegible]
$UICl_2$	$UCl_2I_2 \longrightarrow UICl_2 + \frac{1}{2}I_2$	(750)		Stable	(700)			
UI_2Cl	$UCl_3 + 2UI_3$	(725)		Stable	(700)			
$UIBr_2$	$UI_2Br_2 \longrightarrow UIBr_2 + \frac{1}{2}I_2$	(700)		Stable	(700)			
UI_2Br	$UI_3Br \longrightarrow UI_2Br + \frac{1}{2}I_2$	(690)		Stable	(700)			

At 315°C, the reaction is slow and many hours are required for its completion. Treatment of UF_3 with HCl does not give any $UClF_3$.

An x-ray diffraction pattern of an impure sample indicated that $UClF_3$ has a cubic structure with $a_1 = 8.64$ Å. The compound is rather stable and gives off no chlorine when heated in argon to 400°C. It is, however, non-volatile.

(b) Uranium Dichlorodifluoride, UCl_2F_2. This compound was first prepared (TEC - CEW 1, 2) by the reaction:

$$UO_2F_2 + 2CCl_4 \longrightarrow UCl_2F_2 + 2COCl_2 + Cl_2 \tag{33}$$

The reaction may be effected either in the liquid phase under pressure at 130°C or in the vapor phase at 450°C. Of these the vapor phase reaction is more convenient. It is interesting to note that the liquid phase reaction produces a small amount of carbon tetrachloride-soluble material, and it has been suggested that it is a pentavalent, mixed halide such as UCl_3F_2 or UCl_4F. However, compounds of this type have not as yet been definitely identified. UCl_2F_2 dissolves in water to give chloride and flouride ions indicating that the compound is not a mechanical mixture of UCl_4 and UF_4, since UF_4 is insoluble in water. On heating, UCl_2F_2 undergoes disproportionation:

$$2UCl_2F_2 \longrightarrow UF_4 + UCl_4 \tag{34}$$

The UCl_4 can be removed by vacuum distillation (TEC -CEW 1, 2). The mixed halide as such cannot be distilled.

Several attempts (MP Ames 31; UCRL 14) have been made to prepare UCl_2F_2 by the reaction:

(35) $$UCl_4 + UF_4 \longrightarrow 2UCl_2F_2$$

On the basis of fragmentary observations, it seems that UCl_2F_2 does form and that it melts at about 460°C. However, the product obtained in this way is less pure than that obtained by reaction of UO_2F_2 with CCl_4, probably because of the higher temperature used.

(c) Uranium Monobromotrifluoride, $UBrF_3$ (MP Ames 31). $UBrF_3$ can be prepared in the same way as the corresponding chlorine compound:

(36) $$UF_3 + \frac{1}{2}Br_2 \longrightarrow UBrF_3$$

Thus, bromine vapor may be carried in a stream of helium over UF_3 at 250°C. Usually mixtures of $UBrF_3$ and UF_3 result unless the reaction is continued for very long periods. The compound $UBrF_3$ is stable in helium to 450°C; hydrogen at 200°-400°C slowly reduces it to UF_3.

(d) Uranium Monoiodotrifluoride UIF_3 (MP Ames 31). Iodine vapor (carried in helium) reacts at 180°C with UF_4 to give mixtures of UF_3 and UIF_3. The mixture is brownish-black in color, hygroscopic, and evolves iodine at room temperature in air. It appears to be stable to 100°C in the absence of air or moisture. This compound is imperfectly identified.

None of the chloro-, bromo-, or iodofluorides can be volatilized without decomposition.

4.2. Uranium(IV) Bromo- and Iodochlorides. These compounds have been studied in more detail than all the mixed halides of uranium. Data are now available on the vapor pressures, heats of formation and crystal chemistry of some of the members of this group. Their identity has been well established, but more extensive x-ray data would be desirable.

(a) Uranium Monobromotrichloride, $UBrCl_3$ (UCRL 14, 15, 16). This compound is best prepared by bromination of UCl_3:

(37) $$UCl_3 + \tfrac{1}{2}Br_2 \longrightarrow UBrCl_3$$

The reaction is carried out by heating UCl_3 in a closed system to 500°C in contact with bromine vapors. Since the rate of bromination is strongly dependent on the partial pressure of bromine, the latter is maintained at its equilibrium value over liquid bromine at room temperature. The product is purified by sublimation.

With liquid bromine the rate of reaction (37) at 125°C is too slow to be of practical use.

A number of other methods have also been explored. Fairly good results can be obtained by fusion of UBr_4 and UCl_4:

(38) $$UBr_4 + 3UCl_4 \longrightarrow 4UBrCl_3$$

However, the product of sublimation contains as much as 20 per cent UCl_4. The same type of reaction has been applied to UCl_3 and UBr_4:

(39) $$UCl_3 + UBr_4 \rightleftharpoons UBrCl_3 + UBr_3$$

Reaction occurs at 550°C, but apparently an equilibrium is established; the product obtained by subliming the reaction product is a mixture of $UBrCl_3$ and UBr_4. This reaction is therefore unsuitable for the preparation of pure $UBrCl_3$.

Another approach which has been partially explored is the decomposition of complex compounds of UCl_4 and NaBr. On heating NaBr and UCl_4 to 500°C, a compound, probably $Na_2UCl_4Br_2$ is formed. Subliming this compound in vacuum gives a mixture of UCl_4 (25 per cent) and $UBrCl_3$ (75 per cent). When NaBr and UCl_4 are fused at 700°C and sublimed in vacuum, a mixture of 73 per cent $UBrCl_3$ and 27 per cent UBr_2Cl_2 is obtained. The following reactions are postulated to explain these results:

(40) $$UCl_4 + 2NaBr \rightleftharpoons Na_2UBr_2Cl_4$$

(41) $$Na_2UBr_2Cl_4 \longrightarrow UBrCl_3 + NaBr + NaCl$$

(42) $$UBrCl_3 + 2NaBr \rightleftharpoons Na_2UBr_3Cl_3$$

(43) $$Na_2UBr_3Cl_3 \longrightarrow UBr_2Cl_2 + NaBr + NaCl$$

The compound $Na_2UBr_4Cl_2$ can be prepared in similar fashion, but yields only a mixture of UBr_3Cl and UBr_2Cl_2 on sublimation.

$UBrCl_3$ is a hygroscopic, dark green crystalline substance which resembles UCl_4 in most respects. It dissolves readily in water to give a green solution from which bromine may be displaced by addition of HNO_3. The compound melts at 521°C with an estimated heat of fusion of 11.6 kcal/mole. Treatment with hydrogen at 400°-500°C results in the formation of approximately 70 mole per cent $UBrCl_2$ and 30 mole per cent UCl_3. The thermodynamics of this equilibrium is discussed below.

The compound is thermally stable and can be sublimed in vacuum without decomposition. It is stable in dry air, but it reacts very readily with water vapor to form oxyhalides.

A preliminary examination of the crystal structure of $UBrCl_3$ has been made (MP Ames 9, 32), but unfortunately the work was confined to preparations of rather indefinite composition. $UBrCl_3$ apparently possesses a tetragonal structure very similar to UCl_4, with $a_1 = 8.434$ Å, $a_3 = 7.690$ Å and a unit cell slightly larger than pure UCl_4. The pattern suggests that the mixed halide is not truly body-centered, and that the replacement of chlorine in the lattice is not random.

(b) Uranium(IV) Dibromodichloride, UBr_2Cl_2 (UCRL 16). UBr_2Cl_2 is best prepared by fusion (at 590°C) of an equimolar mixture of UCl_4 and UBr_4 in a quartz tube for about three days. The reaction is carried out in an atmosphere of helium, and on completion of the heating period about three-quarters of the charge is usually found to have sublimed. The product is a dark-green crystalline substance, and has the composition UBr_2Cl_2 (containing approximately 1 per cent excess UCl_4). The composition of the sublimate indicates a compound rather than a mixture of UCl_4 and UBr_4 since these two substances possess very different vapor pressures and sublimate from an equimolar mixture would be much richer in bromine than is actually the case.

In its appearance, UBr_2Cl_2 resembles UCl_4 more closely than UBr_4. It melts at 510°C with an estimated heat of fusion of 12.3 kcal/mole. The boiling point (calculated from vapor pressure data, see below) is 780°C. Reduction with hydrogen (350°-450°C) yields a mixture of roughly 60 per cent UBr_2Cl and 40 per cent $UBrCl_2$; the thermodynamics of the reduction is discussed on p. . UBr_2Cl_2 is thermally stable and can be sublimed in vacuum without decomposition. It is stable in dry air, but must be preserved from traces of moisture since it is

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very hygroscopic.

(c) Uranium(IV) Tribromomonochloride, UBr_3Cl. Heating a mixture of UCl_4 and UBr_4 (mole ratio 1:3) to 590°C for one day in an helium atmosphere yields sublimation product of the composition UBr_3Cl. Direct chlorination of UBr_3 leads only to UCl_4. As expected, UBr_3Cl resembles UBr_4 more closely than UCl_4. It is a light brown substance melting at 502°C with a heat of fusion of 13.6 kcal/mole (UCRL 13). UBr_3Cl may be sublimed in vacuum without decomposition. Hydrogen at 350°-450°C results in the formation of 40 per cent UBr_3 and 60 per cent UBr_2Cl.

(d) Uranium(IV) Monoiodotrichloride, $UICl_3$ (UCRL 15). This compound is rather difficult to prepare in pure form because of its thermal instability. It can be obtained by iodination of UCl_3:

$$UCl_3 + \tfrac{1}{2}I_2 \xrightleftharpoons{500^\circ C} UICl_3 \qquad (44)$$

$UICl_3$ appears to be stable in the vapor phase even at 500°C. Decomposition occurs, however, when solid is deposited; it is essential, therefore, to maintain the partial pressure of the iodine in the system above the dissociation pressure of $UICl_3$.

$UICl_3$ is a reddish brown to black substance which loses iodine even at 225°C in vacuum. The decomposition pressures range from 5×10^{-4} mm Hg at 200°C to 1.34×10^{-1} mm Hg at 302°C. Decomposition is too extensive to permit vapor pressure measurements, but the indications are that the compound has a vapor pressure greater than that of UCl_4 and probably quite similar to that of UI_4.

The compound is extraordinarily hygroscopic. Moist air liberates iodine and forms oxyhalide. $UICl_3$ must, therefore, be preserved from all contact with air or moisture.

(e) <u>Uranium(IV) Diiododichloride, UI_2Cl_2</u>. This compound can be prepared in the same way as UBr_2Cl_2. By fusion of an equimolar mixture of UCl_4 and UI_4 (in the presence of a small amount of iodine to minimize decomposition of the UI_4): (UCRL 13)

(45) $$UCl_4 + UI_4 \longrightarrow 2UI_2Cl_2$$

UI_2Cl_2 is a black crystalline substance. It is distinctly more stable than $UICl_3$. The vapor pressure and melting point of UI_2Cl_2 and $UICl_3$ appear to be quite similar.

(f) <u>Uranium(IV) Triiodomonochloride, UI_3Cl</u>. This compound has been prepared by fusion of UCl_4 and UI_3 above the melting point of UCl_4: (UCRL 14)

(46) $$UI_3 + UCl_4 \xrightarrow{600^\circ C} UI_3Cl + UCl_3$$

After sublimation material containing over 90 per cent UI_3Cl is obtained, with UCl_3 as the most persistent contaminant. The presence of the latter in the sublimate is due to a small amount of free iodine which is formed through unavoidable exposure of the starting material (UI_3) to air and moisture. This iodine converts UCl_3 to $UICl_3$, which sublimes together with UI_3Cl but decomposes back into UCl_3 and I_2 upon condensation.

UI_3Cl is a black crystalline substance with a red cast in the finely divided state. It is much more stable than $UICl_3$ or any of the other iodochlorides, and can be sublimed without apparent decomposition with a low partial pressure (0.1 mm Hg) of iodine vapor in the system.

It appears to be slightly more volatile than UBr_4.

4.3. Uranium(IV) Iodobromides. All three possible members of this class are known. They are relatively unstable compounds which lose iodine rather easily. $UIBr_3$ is the only member of the group which can be sublimed without decomposition. A comparison of the order of thermal stability of the iodobromides with that of the iodochlorides is of interest (Table 13).

TABLE 13

THERMAL STABILITY OF IODOCHLORIDES AND IODOBROMIDES

Stability	Iodochlorides	Iodobromides
Decreasing Stability	UI_3Cl	$UIBr_3$
	UI_2Cl_2	UI_2Br_2
	$UICl_3$	UI_3Br

All of the iodobromides are extremely hygroscopic and must be prepared and stored in the complete absence of air or moisture. They are all black, crystalline substances.

(a) Uranium(IV) Monoiodotribromide, $UIBr_3$. This compound is best prepared by the reaction:

$$UBr_3 + \tfrac{1}{2}I_2 \xrightarrow{500^{\circ}C} UIBr_3 \quad (47)$$

A partial pressure of 0.5 mm Hg of iodine is maintained during cooling. This method succeeds because $UIBr_3$ is much more stable than the corresponding chlorine compound, $UICl_3$ (for whose preparation this method is quite inappropriate).

$UIBr_3$ is volatile and has an appreciable vapor pressure (1×10^{-2} mm Hg) at 375°C; it may be sublimed without decomposition in a system in which $P(I_2) = 0.1$ mm Hg. Decomposition to UBr_3 and iodine occurs at 400°C in vacuum. $UIBr_3$ melts at 478°C.

(b) <u>Uranium(IV) Diiododibromide, UI_2Br_2.</u> The most convenient method of preparation is the fusion of equivalent quantities of UI_4 and UBr_4:

(48) $$UI_4 + UBr_4 \longrightarrow 2UI_2Br_2$$

Qualitatively, this compound resembles $UIBr_3$ closely except for a much lesser thermal stability.

(c) <u>Uranium(IV) Triiodomonobromide, UI_3Br.</u> Fusion of a mixture of UI_4 and UBr_4 in appropriate proportions leads to the formation of this compound:

(49) $$UBr_4 + 3UI_4 \longrightarrow 4UI_3Br$$

The product is sublimed from the reaction zone. The compound is thermally unstable and undergoes ready conversion to UI_2Br and iodine at 300°C. Its thermal stability is comparable to that of UI_2Br_2.

<u>4.4. Uranium(IV) Halides Containing Three Different Halogens.</u>

The compounds $UIBrCl_2$ and $UIBr_2Cl$ have not been prepared in pure form. However, mixtures of the two have been obtained by the following reactions:

(50) $$2UBr_2Cl_2 + H_2 \longrightarrow UBrCl_2 + UBr_2Cl + HBr + HCl$$

Iodination of the product then gives:

(51) $$UBrCl_2 + UBr_2Cl + I_2 \longrightarrow UIBrCl_2 + UIBr_2Cl$$

There is reason to believe that $UIBr_2Cl$ is more stable than $UIBrCl_2$ with respect to loss of iodine.

4.5. Uranium(III) Mixed Halides. Mixed halides of trivalent uranium can be prepared by (a) thermal decomposition of mixed U(IV) halides, (b) reduction of mixed U(IV) halides by hydrogen and (c) fusion of a mixture of two U(III) halides.

All mixed U(III) halides are black crystalline substances which resemble UCl_3 and UI_3 with respect to thermal stability, volatility, etc. Little is known of their physical or chemical properties. The reduction of the U(IV) halides with hydrogen, however, has permitted the calculation of thermodynamic constants for $UBrCl_2$ and UBr_2Cl (cf. p.).

(a) Uranium(III) Monobromodichloride, $UBrCl_2$. Reduction of $UBrCl_3$ with hydrogen produces a mixture of $UBrCl_2$ and UCl_3. Iodination of this mixture removes the UCl_3 (as volatile $UICl_3$). The best method for preparing $UBrCl_2$, however, is fusion of UCl_3 and UBr_3:

(52) $$2UCl_3 + UBr_3 \xrightarrow{850^\circ C} 3UBrCl_2$$

The product can be purified from unreacted trichloride by treatment with iodine vapor and sublimation of the $UICl_3$ formed.

(b) Uranium(III) Dibromomonochloride, UBr_2Cl. This compound has been prepared by reduction of UBr_3Cl with hydrogen. The mixture of UBr_2Cl and UBr_3 which is produced in this way is treated with iodine; the $UIBr_3$ and $UIBr_2Cl$ vapors are then passed through a tube heated to 385°C in a stream of iodine vapor of 0.1 mm Hg pressure. The $UIBr_2Cl$

decomposes under these conditions to UBr_2Cl, while the more stable $UIBr_3$ sublimes away.

Fusion of UBr_3 and UCl_3 (1:2) should also yield UBr_2Cl.

(c) Uranium(III) Monoiododichloride, $UICl_2$. Thermal decomposition of UI_2Cl_2 in vacuum yields pure $UICl_2$.

(d) Uranium(III) Monoiododibromide, $UIBr_2$. This compound is obtainable by the thermal decomposition of UI_2Br_2 in vacuum.

(e) Uranium(III) Diiodomonobromide, UI_2Br. This compound may be readily prepared by the thermal decomposition of UI_3Br in vacuum.

All these compounds dissolve in water to give a red solution. They are hygroscopic but not to the same extent as the U(IV) compounds.

4.6. Vapor Pressure Measurements. The vapor pressures of $UBrCl_3$ (UCRL 17), UBr_3Cl (UCRL 18), UBr_2Cl_2 (UCRL 19) and $UIBr_3$ (UCRL 20) have been studied by a molecular effusion method. Tables 13-a and 14 summarize the experimental data.

TABLE 13 a*

VAPOR PRESSURE EQUATIONS FOR SOME U(IV) MIXED HALIDES

$$\log P_{\text{mm Hg}} = A - \frac{B}{T}$$

Compound	A	B	Temperature Range (°C)
$UBrCl_3$	13.852	10526	320-430
UBr_2Cl_2	13.149	9901	330-404
UBr_3Cl	13.280	10000	320-420
$UIBr_3$	13.416	9901	315.382

* (UCRL 3).

TABLE 14

INTERPOLATED VAPOR PRESSURE OF SOME U(IV) MIXED HALIDES

Compound T °C	$UBrCl_3$	UBr_2Cl_2	UBr_3Cl	$UIBr_3$
320	1.25×10^{-4}	2.85×10^{-4}	2.57×10^{-4}	5.25×10^{-4}
330	2.48×10^{-4}	5.42×10^{-4}	4.95×10^{-4}	9.93×10^{-4}
340	4.75×10^{-4}	1.00×10^{-3}	9.30×10^{-4}	1.84×10^{-3}
350	9.00×10^{-4}	1.82×10^{-3}	1.70×10^{-3}	3.34×10^{-3}
360	1.66×10^{-3}	3.23×10^{-3}	3.02×10^{-3}	5.96×10^{-3}
370	3.00×10^{-3}	5.70×10^{-3}	5.40×10^{-3}	1.04×10^{-2}
380	5.40×10^{-3}	9.80×10^{-3}	9.40×10^{-3}	1.79×10^{-2}
390	9.50×10^{-3}	1.67×10^{-2}	1.61×10^{-2}	
400	1.64×10^{-2}	2.77×10^{-2}	2.69×10^{-2}	
410	2.80×10^{-2}	4.62×10^{-2}	4.50×10^{-2}	
420	4.70×10^{-2}		7.30×10^{-2}	
430	7.90×10^{-2}			

The heats and free energies of sublimation are given in Table 15.

TABLE 15

HEATS AND FREE ENERGIES OF SUBLIMATION OF SOME U(IV) MIXED HALIDES

$$\Delta F_{subl.} = \Delta H_o + AT \log T - BT$$

Compound	$\Delta H_{sublimation}$ (kcal/mole)	ΔH_o (cal/mole)	A	B
$UBrCl_3$	48.5	57692	36.85	168.5
UBr_2Cl_2	45.5	56000	36.85	167.1
UBr_3Cl	46.3	54474	34.55	158.2
$UIBr_3$	43.0	51417	34.55	154.7

4.7. Thermochemistry. Heats of solution, dissociation pressures and reduction equilibria with hydrogen have been measured for seven mixed halides and permit calculation of the heat and free energy of formation and entropy of these compounds. No specific heat data are available and the consequent uncertainties in the assumed ΔC_p for the reduction equilibria are reflected in the final values.

(a) Reduction Equilibria (UCRL 21). The results of measurements of the reduction equilibria are summarized in Table 17.

TABLE 17

EQUILIBRIA OF REDUCTION OF MIXED HALIDES WITH HYDROGEN

	Reaction	$\Delta H_{700°K}$ (kcal/mole)	$\Delta F^{o}_{700°K}$ (kcal/mole)	$\Delta S_{700°K}$ (e.u.)
(53)	$UBrCl_{3(s)} + \frac{1}{2}H_{2(g)} \rightleftharpoons$ $UBrCl_{2(s)} + HCl_{(g)}$	16.2	1.73	20.67
(54)	$UBrCl_{3(s)} + \frac{1}{2}H_{2(g)} \rightleftharpoons$ $UCl_{3(s)} + HBr_{(g)}$	16.3	2.98	20.03
(55)	$UBr_2Cl_{2(s)} + \frac{1}{2}H_{2(g)} \rightleftharpoons$ $UBr_2Cl_{(s)} + HCl_{(g)}$	17.6	2.68	21.62
(56)	$UBr_2Cl_{2(s)} + \frac{1}{2}H_{2(g)} \rightleftharpoons$ $UBr\ Cl_{2(s)} + HBr_{(g)}$	16.9	3.18	20.03
(57)	$UBr_3Cl_{(s)} + \frac{1}{2}H_{2(g)} \rightleftharpoons$ $UBr_{3(s)} + HCl_{(g)}$	17.1	3.61	19.84
(58)	$UBr_3Cl_{(s)} + \frac{1}{2}H_{2(g)} \rightleftharpoons$ $UBr_2Cl_{(s)} + HBr_{(g)}$	16.9	2.98	20.47

(b) Decomposition Pressures of Iodine over $UIBr_3$ (UCRL 22) and $UICl_3$ (UCRL 20). The decomposition pressure of iodine as a function of temperature has been measured for these two compounds. The results are summarized in Table 18.

TABLE 18

IODINE PRESSURE ABOVE $UICl_3$ AND $UIBr_3$

$UICl_3$		$UIBr_3$	
Temperature (°C)	Iodine Pressure (mm Hg)	Temperature (°C)	Iodine Pressure (mm Hg)
198.6	4.73×10^{-4}	277.3	5.44×10^{-4}
221.3	2.09×10^{-3}	293.2	1.20×10^{-3}
241.0	6.64×10^{-3}	314.9	3.05×10^{-3}
261.7	1.70×10^{-2}	331.1	6.18×10^{-3}
280.0	5.07×10^{-2}	349.7	1.49×10^{-2}
302.0	1.35×10^{-1}	368.2	2.44×10^{-2}
		381.4	3.75×10^{-2}

(c) Thermodynamic Constants. These constants have been determined for seven mixed halides. The results were given in Table 12. For details of the calculations, we refer to the paper by G. MacWood in Volume 11B.

5. Uranium (IV) Borohydride, $U(BH_4)_4$ (U. of Chicago, Dept. of Chem. 1, 2)

Some of the successful methods for separating isotopes require the use of volatile compounds. Uranium hexafluoride is the only known compound of uranium which possesses an appreciable vapor pressure at room temperature, and it has, therefore, been extensively utilized in isotope separations. The great chemical reactivity of uranium hexafluoride, however, gives rise to serious corrosion problems, and consequently much effort has been devoted to preparing non-corrosive volatile uranium compounds. Efforts to prepare uranium carbonyls have so far proved unsuccessful. Volatile organic chelate compounds have been prepared; the vapor pressures of such compounds, however, are low-- in the vicinity of 10^{-3} mm Hg at room temperature for the most volatile members of the class. Furthermore, the molecular weight of these organic compounds is much higher than that of uranium hexafluoride, while for many purposes a low molecular weight is essential. The discovery of uranium borohydride has indicated one possible way of solving the problem, and has also opened what promises to be a very interesting chapter in uranium chemistry.

The metal borohydrides are a relatively new class of compounds. They can be considered as "pseudo-halides", with the radical BH_4 playing the part of a halide, and this justifies their treatment in the present chapter.

Prior to the discovery of uranium borohydride the borohydrides of lithium, beryllium and aluminum were known (Schlesinger, 1939, 1940; Burg, 1940). These compounds were first made by the action of diborane on an alkyl compound of the metal:

(59) $$2LiC_2H_5 + 2B_2H_6 \longrightarrow 2LiBH_4 + (C_2H_5)_2B_2H_4$$

(60) $$Be(C_2H_5)_2 + 2B_2H_6 \longrightarrow Be(BH_4)_2 + (C_2H_5)_2B_2H_4$$

(61) $$2Al(C_2H_5)_3 + 6B_2H_6 \longrightarrow 2Al(BH_4)_3 + 3(C_2H_5)_2B_2H_4$$

The reactions are more complex than represented by the equations since trialkyl boron compounds are produced in the early stages and complex mixtures of alkyl diboranes in the latter stages. Lithium and beryllium borohydrides are salt-like but aluminum borohydride is a typical non-polar substance. It is a volatile liquid (b.p. 44.5°C) soluble in benzene. Since beryllium borohydride and aluminum borohydride are the most volatile of all known compounds of these metals, it seemed worthwhile to try to prepare the corresponding compound of uranium.

5.1. Preparation of Intermediates. Unlike the other borohydrides, uranium(IV) borohydride cannot be prepared by the reaction of metal alkyls with diborane, since uranium alkyls are unknown. The best method of preparation found so far is the reaction of aluminum borohydride with uranium tetrafluoride. The method for preparing $Al(BH_4)_3$ described in the literature is very tedious and suitable only for the preparation of very small amounts. It was necessary, therefore, to devise more practical methods for the preparation of $Al(BH_4)_3$. The detailed results of this interesting work are to appear elsewhere. The following reactions may be employed in preparing aluminum borohydride:

(62) $$NaH + B(OCH_3)_3 \longrightarrow NaBH(OCH_3)_3$$

(63) $$2NaBH(OCH_3)_3 + B_2H_6 \longrightarrow 2NaBH_4 + B(OCH_3)_3$$

(64) $$3NaBH_4 + AlCl_3 \longrightarrow Al(BH_4)_3 + 3\ NaCl$$

Diborane can be prepared by (MP Chicago 11) one of the following two reactions:

(65) $$6LiH + 8(C_2H_5)_2O{:}BF_3 \longrightarrow B_2H_6 + 6LiBF_4 + 8(C_2H_5)_2O$$

or,

(66) $$6NaBH(OCH_3)_3 + 8(C_2H_5)_2O{:}BF_3 \longrightarrow B_2H_6 + 6NaBF_4 + 6B(OCH_3)_3 + 8(C_2H_5)_2O$$

5.2. Preparation of Uranium(IV) Borohydride. Uranium(IV) borohydride is formed by treating UF_4 with $Al(BH_4)_3$. Reaction is spontaneous (and exothermal) at room temperature. It proceeds according to the equation:

(67) $$UF_4 + 2Al(BH_4)_3 \longrightarrow U(BH_4)_4 + 2Al(BH_4)F_2$$

The uranium tetrafluoride in this reaction is best prepared by dehydration of $2UF_4{\cdot}5H_2O$ (cf. Chapter 12). Final dehydration is accomplished just before use: Uranium tetrafluoride monohydrate is attached to a vacuum line and dehydrated at 350°C at 10^{-5} mm Hg; aluminum borohydride is then distilled into the reaction tube which is then sealed off from the vacuum line. Since considerable heat is evolved in reaction (67), it is advisable to place the reaction tube in an ice-salt mixture for several hours and then to allow the reaction to go to completion at room temperature. The reaction tube is then joined again to the vacuum line through a breaker seal and the $U(BH_4)_4$ and excess $Al(BH_4)_3$ are distilled away. The $U(BH_4)_4$ is trapped in a U-tube at -20°C, and the $Al(BH_4)_3$ in a U-tube immersed in liquid nitrogen. With large quantities (25 g) the sublimation may require many hours, the necessary time greatly depending on the diameter of the tubing.[1] Eighty to ninety per cent yields of $U(BH_4)_4$ (calculated in relation to the UF_4 used) can be attained.

Efforts have been made to devise procedures which would not require the use of the highly inflammable $Al(BH_4)_3$. The only procedure which so far offers any promise is the reaction of UF_4 with $LiBH_4$ in ether. Evidence for the production of $U(BH_4)_4$ by this reaction was obtained, but neither the yield nor the purity of the product was satisfactory. Further research is indicated. A number of other reactions were investigated but proved unsuccessful. Among these were:

(a) Action of $Al(BH_4)_3$ on UCl_4. A little $U(BH_4)_4$ was obtained, but the bulk of the uranium appeared to have been reduced to the trivalent state.

(b) Action of $LiBH_4$, $NaBH_4$, KBH_4 on UF_4 or UCl_4 at Temperatures up to 125°C in the Absence of Solvents. No $U(BH_4)_4$ was obtained.

(c) Action of Diborane, or Borine Carbonyl, $BH_3.CO$ (Burg, 1937), on Uranium Metal or Uranium Hydride. No reaction resulted under a wide range of temperatures and pressures. It is certain, however, that both the uranium metal and the hydride were impure and re-examination is desirable.

The formula of uranium(IV) borohydride was established by hydrolysis:

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[1] The non-volatile residue from the reaction is spontaneously and violently inflammable in air; the residue must be hydrolyzed by slowly admitting water vapor before air is allowed to enter the reaction vessel.

(68) $$U(BH_4)_4 + 16H_2O \longrightarrow U(OH)_4 + 4H_3BO_3 + 16H_2\uparrow$$

The hydrogen was measured with a Toepler pump, the boron was determined as methyl borate after distillation, by titration with $Ba(OH)_2$ and mannitol, and the uranium as U_3O_8. The experimental results lead to the formula $U_{1.0}B_{4.0}H_{16.1}$ or $U(BH_4)_4$.

5.3. Preparation of Alkyl Derivatives of Uranium(IV) Borohydride. Treatment of $U(BH_4)_4$ with boron trimethyl in an evacuated, sealed vessel at 50° to 70°C results in the formation of a green, moderately viscous liquid together with a small amount of a brown non-volatile solid. This reaction proceeds slowly below 50°C. From the mixture two volatile uranium compounds have been isolated. The less volatile is a crystalline solid, colorless in thin layers, lavender to almost black in thicker crystals. The more volatile compound, after purification by fractional sublimation, is a green solid. The difference in volatility is sufficiently great to permit partial separation by fractional distillation and sublimation, as the green substance passes through a trap maintained at -10°C where the lavender material is condensed. Separation is incomplete, but treatment of the lavender substance with excess boron trimethyl removes the last traces of the green material. The green substance can be obtained in the pure state by treating the impure product with excess diborane at 30°-40° C. The rationale of these treatments are apparent from the structures of these two substances, which were established by analysis and by reaction with water and hydrogen chloride (see Sec. 5; 5 c below). The green substance gave with hydrogen chloride both diborane and methyl boron chlorides (chiefly CH_3BCl_2); the lavender compound gave no diborane. Neither compound produced any methane. Therefore the compounds clearly contain carbon as methyl groups. It is reasonable to conclude that in both the methyl groups are attached to boron and not to uranium, that in the lavender compound there are no (BH_4) groups, and that each carbon is attached to a different boron atom. In conjunction with the analytical data and molecular weight determinations, the results strongly suggest that the green compound is monomethyl uranium borohydride, $U(BH_4)_3(BH_3CH_3)$ and the lavender compound is tetramethyl uranium borohydride, $U(BH_3CH_3)_4$. The methods of purification mentioned above were based on the premise that $B(CH_3)_3$ will alkylate traces of the monomethyl compound present in tetramethyl borohydride, and that diborane will dealkylate traces of tetramethyl compound which may be present in the monomethyl derivative.

Boron triethyl reacts with $U(BH_4)_4$ in the same way as $B(CH_3)_3$, but it has not been possible to isolate pure compounds from the reaction mixture. The same is true of the higher boron alkyls which also react with $U(BH_4)_4$ but which yield reaction mixtures hitherto defying separation. The volatility of the ethyl or higher alkyl uranium borohydrides apparently is much less than that of the methyl compounds.

5.4. Physical Properties of Uranium(IV) Borohydrides. Vapor pressures were determined by means of a glass Bourdon gauge in an all-glass system. Vapor pressure data are summarized in Tables 19 and 20. The same apparatus was used for determining the molecular weight. The molecular weight determinations showed the compounds to be monomers.

TABLE 19

VALUES OF CONSTANTS FOR EQUATIONS REPRODUCING THE OBSERVED VAPOR PRESSURES OF URANIUM BOROHYDRIDES

$$\ln p = B - \frac{A}{T}$$

Substance	A	B
$U(BH_4)_4$	4,264.6	13.354
$U(BH_4)_3(BH_3CH_3)$	3,150.0	10.679
$U(BH_3CH_3)_4$	2,970.0	8.820

TABLE 20

INTERPOLATED VAPOR PRESSURE OF $U(BH_4)_4$ AND ITS DERIVATIVES

Temperature	Pressure (mm Hg)		
(°C)	$U(BH_4)_4$	$U(BH_4)_3(BH_3CH_3)$	$U(BH_3CH_3)_4$
30	0.19	1.92	0.10
35	0.33	2.83	0.15
40	0.54	4.12	0.21
45	0.89	5.93	0.30
50	1.43	8.45	0.42
55	2.27	11.89	0.58
60	3.56	16.48	0.80
65	5.51	22.91	1.08
70[a]	8.40	31.26	1.45
75[a]	12.68	42.36	1.93

[a] Represent considerable extrapolation.

$U(BH_4)_4$ sublimes without melting; it melts at 126°C with extensive decomposition. The melting point of $U(BH_3CH_3)_4$ is approximately 72°-74°C. The melting point of the monomethyl compound is in doubt. A melting point of 95°C has been observed, but on a sample in which disproportionation to $U(BH_4)_4$ and more highly methylated products may have occurred.

Photochemical Properties (Columbia 1, 2). $U(BH_4)_4$ vapor decomposes both photochemically and thermally, therefore, the absorption spectrum could be studied only at very low pressures. A continuous band at 21,000 cm^{-1} was found ($p = 4$ mm Hg, $d = 50$ cm).

5.5. Chemical Properties of $U(BH_4)_4$ and its Alkyl Derivatives. Uranium(IV) borohydride is a lustrous, green crystalline material, which in large aggregates appears almost black. As mentioned before, the monomethyl compound is also green, while the tetramethyl compound forms lavender crystals.

(a) Solubility. Water and alcohol react vigorously with $U(BH_4)_4$. $U(BH_4)_4$ is soluble in ethyl ether to the extent of 2 g/100 cc at room temperature. The ether cannot be completely removed without decomposition; at -80°C a stable monoetherate, $U(BH_4)_4 \cdot (C_2H_5)_2O$, is formed. Non-polar solvents such as n-heptane dissolve $U(BH_4)_4$ slowly and to only a slight extent; the borohydride can be recovered unchanged from such solvents. Highly purified benzene does not react with $U(BH_4)_4$, but it is difficult to remove the benzene without decomposition of borohydride. The solubility in benzene is too small for practical purposes. The solubility of the alkyl derivatives has not been determined.

(b) Air. $U(BH_4)_4$ reacts with dry air slowly. Yellow non-volatile products not further investigated are formed. The compound can be exposed to dry air for short periods without hazard.

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(c) Hydrolytic Reactions.

$$U(BH_4)_4 + 16H_2O \longrightarrow U(OH)_4 + 4H_3BO_3 + 16H_2 \tag{69}$$

$$U(BH_4)_4 + 4HCl \longrightarrow UCl_4 + 2B_2H_6 + 4H_2 \tag{70}$$

$$U(BH_4)_4 + 16CH_3OH \longrightarrow U(OCH_3)_4 + 4B(OCH_3)_3 + 16H_2 \tag{71}$$

The alkylated borohydrides react in similar fashion:

$$U(BH_4)_3(BH_3CH_3) + 6HCl \longrightarrow UCl_4 + 3/2\ B_2H_6 + CH_3BCl_2 + 6H_2 \tag{72}$$

$$U(BH_3CH_3)_4 + 12HCl \longrightarrow UCl_4 + 4CH_3BCl_2 + 12H_2 \tag{73}$$

(d) Diborane. At room temperature, B_2H_6 does not react with $U(BH_4)_4$:

$$U(BH_4)_4 + B_2H_6 \longrightarrow n.a. \tag{74}$$

The alkyl borohydrides are converted to the simple borohydride:

$$U(BH_4)_3(BH_3CH_3) + B_2H_6 \longrightarrow U(BH_4)_4 + CH_3BH_2BH_3 \tag{75}$$

$$U(BH_3CH_3)_4 + B_2H_6 \longrightarrow U(BH_4)_4 + (CH_3)_4B_2H_2 \tag{76}$$

(e) Methyl Borate. Reaction occurs when $U(BH_4)_4$ is treated with $B(OCH_3)_3$ at 70°C for one hour. The products are distinctly less volatile than $U(BH_4)_4$. The reaction is complex, as H_2, B_2H_6 and dimethoxyborine, $BH(OCH_3)_2$, are obtained in addition to the main solid product. Analysis suggests the white solid product to be a mono-methoxy derivative, $U(BH_4)_3(BH_3OCH_3)$.

(f) Boron Alkyls and other Metal Alkyls. The reaction of $U(BH_4)_4$ and $B(CH_3)_3$ to give methyl derivatives of the simple borohydride has already been discussed. Zinc methyl, $Zn(CH_3)_2$, and aluminum methyl,

$Al(CH_3)_3$, cause extensive decomposition of $U(BH_4)_4$ at 50°C. The black solid which forms has not been further investigated.

(g) Lithium Ethyl. Since it is known that the reaction

$$3LiC_2H_5 + Al(BH_4)_3 \longrightarrow 3LiBH_4 + Al(C_2H_5)_3 \tag{77}$$

takes place readily, it appeared reasonable to apply this reaction to the problem of preparing uranium alkyl derivatives:

$$U(BH_4)_4 + xLiC_2H_5 \longrightarrow U(BH_4)_{4-x}(C_2H_5)_x + xLiBH_4 \tag{78}$$

In benzene solution, however a black non-volatile material forms, apparently as a result of reduction, and no evidence for the formation of U - C bonds has been found.

(h) Carbon Monoxide (Ethyl Corporation 1). Carbon monoxide does not react with $U(BH_4)_4$ at 50°C. At 80°C reaction occurs to yield an unknown product considerably less volatile than the original borohydride.

(i) Thermal Stability of the Borohydrides. The decomposition of the borohydrides of uranium occurs most easily in the vapor phase, particularly when the vapors come in contact with solid surfaces. Pyrex glass walls markedly catalyze the decomposition. Metals such as copper or nickel are also very effective in causing decomposition, whereas aluminum and silver are probably less destructive than pyrex.

The kinetics of the decomposition on copper has been studied (Columbia 3). In the presence of freshly reduced copper decomposition occurs at the rate of 7.6×10^{-9} moles/cm^2/hr at 55°C and 10^{-4} mm Hg. The reactions which may occur are:

$$U(BH_4)_4 \longrightarrow U(BH_4)_3 + \tfrac{1}{2}B_2H_6 + \tfrac{1}{2}H_2 \tag{79}$$

$$U(BH_4)_4 \longrightarrow U + 2B_2H_6 + 2H_2 \qquad (30)$$

The amounts of hydrogen and diborane are equal but this, of course, does not permit differentiation between these two possible reactions. Decomposition to uranium boride occurs when vapors of $U(BH_4)_4$ are passed through a heated tube. Beautiful mirrors of uranium boride can be deposited on glass in this way.

5.6. Attempts to Prepare Borohydrides of Hexavalent Uranium.

Uranium hexafluoride, uranium hexachloride, uranium penta- and hexa-methoxides, uranium penta- and hexa-ethoxides and uranium penta-methoxide monoethoxide fail to give a hexavalent borohydride when treated with diborane, borine carbonyl or lithium borohydride. What occurs, is reduction to tetravalent uranium (usually to form uranium(IV) borohydride admixed with other U(IV) compounds), a result which is to be expected in consideration of the strong reducing properties of these boron compounds. Uranium trioxide failed to react with any of the above reagents.

6. Attempted Preparations of a Uranium Carbonyl

The search for volatile compounds of uranium has led to rather intensive efforts to prepare a uranium carbonyl. By analogy to chromium, molybdenum, and tungsten, which are members of the same group in the Periodic Table and which form the volatile compounds, $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$, uranium might be expected to form the compound $U(CO)_6$. The hexacarbonyls of chromium, molybdenum, and tungsten are readily prepared in good yield by a variety of methods. These carbonyls are volatile and surprisingly stable.

In consideration of the possible existence of a uranium hexacarbonyl the "rule" of Sidgwick and Bailey (1934) has been quoted. This rule is based on the hypothesis that each CO group in a metal carbonyl donates two electrons to the central metal atom, and that only those metal carbonyls are stable in which the central metal atom acquires in this way the electronic configuration of a rare gas. Twenty-six electrons would have to enter the electronic sphere of uranium for the latter to acquire the electronic configuration of the hypothetical rare gas which follows it in the Periodic Table. Steric considerations alone would seem to rule out the existence of the resulting compound, $U(CO)_{13}$. This appears as a theoretical argument against the existence of a uranium carbonyl. However, the Sidgwick and Bailey "rule" has no theoretical basis. The acquisition of a rare gas configuration cannot play a decisive role in determining the stability of molecules other than those formed by elements closely preceding or following a rare gas in the Periodic System.

The recent literature pertaining to the metal carbonyls has been reviewed by Hieber (1942), Blanchard(1940) and Trout (1937). These surveys may be consulted for details of the methods of preparation, structure and properties of the carbonyls.

Efforts to prepare uranium carbonyl have been made by three separate groups of workers for the Manhattan Project. Of these the work of the Ethyl Corporation (1) has been most intensive.

6.1. Reaction of Uranium Metal with Carbon Monoxide (Ethyl Corporation 1). Repeated efforts have been made to induce reaction of uranium metal and carbon monoxide under a wide variety of conditions since all of the known metal carbonyls (except that of chromium) have been prepared by direct combination of the metal with carbon monoxide. The following attempted reactions have been reported:

(a) Westinghouse powdered uranium metal (98.6%) was heated with carbon monoxide under a pressure of 2950 psi at 165°C in dry hexane.

(b) The same reaction mixture as (a) was used at 30°C and 2400 psi.

(c) "Activated" uranium metal (prepared by decomposition of the hydride) was treated with CO at a maximum temperature of 114°C and a maximum pressure of 7100 psi.

(d) "Activated" metal (prepared by heating Westinghouse metal to 250°C in vacuo) was reacted with carbon monoxide at 266°C and 8650 psi.

(e) Uranium metal (96% U) was heated in a copper-lined steel cylinder at temperatures up to 200°C and pressures up to 250 atmospheres (British 1).

No formation of a volatile uranium-carbonyl was observed in any of these experiments. It must be pointed out that the metal used was not of a high degree of purity. The finely powdered metal, used by the Ethyl Corporation workers almost certainly had a surface film which could conceivably prevent the reaction. The carbon monoxide contained as much as 0.5 per cent hydrogen and 2.4 per cent nitrogen; that these impurities could have interfered with the desired reaction, especially at the elevated temperatures used, is not impossible.

6.2. Uranium Hydride with Carbon Monoxide (Ethyl Corporation 1) and Nickel Carbonyl. The uranium hydride used in these experiments was prepared from Westinghouse metal. The decomposition pressures of the hydride (3 mm at 225°C, 150 mm at 360°C) reported by the Ethyl Corporation

Group are considerably higher than those reported by other observers (cf. Chapter 11, p.), casting doubt on the identity of the substance used. The hydride was treated with carbon monoxide at temperatures from -180°C to 300°C and pressures up to 8500 psi, with no signs of reaction. Treatment of the "uranium hydride" with $Ni(CO)_4$ (in the presence of $AlCl_3$ or $(CH_3)_2AlCl$) also gave no volatile uranium compound.

6.3. Uranium Halides with Carbon Monoxide and Reducing Agents. A new method for preparing metal carbonyls was discovered by Job and Cassal (1927). It consists of the treatment of the metal halide with a reducing agent in the presence of carbon monoxide. Job and Cassal employed Grignard reagents as reducing agents. The method has been extended by the use of finely divided metals such as silver, copper, cadmium or zinc as reductants (Hieber, 1935; Kocheshkov, 1940). Repeated efforts have been made to obtain a volatile uranium carbonyl by these methods.

(a) (Princeton 4). Uranium tetrachloride was treated with ethyl magnesium bromide and carbon monoxide in an ether-benzene solution. The same reaction was also performed with zinc dust instead of the Grignard reagent. In both cases some carbon monoxide was taken up but no volatile uranium product could be isolated. It is of interest to note that in both cases the reaction mixture was worked up by hydrolysis with water or dilute sulfuric acid; on the apparent presumption that uranium carbonyl, if it exists at all, must not be decomposed by water. (comp. below p.).

(b) (British 1). The above reaction was extended to UO_2Cl_2,

UCl_3, UCl_4, (UCl_4 + UCl_5) mixture, UCl_6 and $U(CH_3COCHCOCH_3)_4$; magnesium methyl iodide, magnesium ethyl bromide, magnesium phenyl bromide, magnesium γ - naphthyl bromide and lithium phenyl bromide were used as Grignard reagents. No volatile uranium compound could be detected. Dimethyl zinc, diethyl zinc, lithium butyl were also used without success (Ethyl Corporation 1).

(c) A number of reactions were carried out in which UCl_4 and UBr_4 were treated with carbon monoxide and zinc dust in acetone solutions. This procedure gives excellent results with $MoCl_5$ but failed to give the desired uranium compound (Ethyl Corporation 1). Apparently reduction to the trivalent state is all that occurs.

6.4. Uranium Halides with Carbon Monoxide and Carriers (Ethyl Corporation 1). A useful procedure for preparing carbonyls is the treatment of an aqueous solution of a metal halide with carbon monoxide in the presence of alkaline potassium cyanide or sodium sulfide (Manchot, 1929; Windsor, 1933; Blanchard, 1934; Hieber, 1939). A few experiments with uranium halides have been performed in which KCN was used as a "carrier" for carbon monoxide but no reaction occurred. Cysteine has also been tried as "carrier" with UCl_3 and CO (Schubert, 1933; Coleman, 1936). Some reaction did occur but the products were not identified. Alkaline hydrogen sulfide or uranyl salts in the presence of carbon monoxide also failed to give a volatile uranium compound (British 1).

6.5. Conclusions. It can be seen from the foregoing discussion that the successful preparation of a volatile uranium carbonyl, or even proof for the existence of such a compound will not be an easy task.

A survey of the recent work shows that most, if not all, of the tested methods for preparing metal carbonyls have been tried. With respect to the work done on metallic uranium it would be very desirable to repeat these experiments using the very pure metal now available, and using pure carbon monoxide. The use of alloys such as nickel-uranium alloy has also been suggested and seems worthy of trial (MP Chicago 12). In all experiments made so for, whenever a reaction occurred (as it frequently did) no attempt was made to ascertain its course. All that was done, was a quick examination to determine whether a volatile uranium compound had been formed. An understanding of just what happens with uranium in some of these reactions might be helpful in planning future experiments.

The methods of working up the reaction mixtures were based on the preparation of $Cr(CO)_6$---a compound which is not sensitive to moisture. It is possible that $U(CO)_6$, if it exists, is sensitive to water. The ability of U(IV) to function as an oxidizing or reducing agent, has not been given sufficient weight in the selection of solvents. Finally, it would perhaps be desirable to re-investigate some of the reactions studied using UCl_5 and UCl_6 rather than UCl_4.

No final conclusions as to the stability of a uranium carbonyl can be drawn from the lack of success hitherto encountered in attempts to prepare such compounds. It must be pointed out, however, that uranium is a strongly electropositive element, and that no carbonyls of elements of the same type such as beryllium or magnesium, are known.

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CHAPTER XVI

URANIUM OXYHALIDES

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URANIUM OXYHALIDES

The oxyhalides of hexavalent uranium of the type of UO_2^{+2} were among the earilest compounds of uranium to be studied. Despite this, few physical constants have been determined with any degree of accuracy, and the chemistry of these compounds is still fragmentary. Until 1940 oxyhalides of uranium (IV) were unknown, but now the compounds $UOCl_2$ and $UOBr_2$ are readily accessible, and a considerable amount of information about them has been accumulated. Evidence for the probable existence of oxyhalides of U(VI) of the type of UO^{+4} and of U(V) of the type of UOX_3, has already been discussed in Chapter XIV.

Here, attention will be directed to the uranyl halides and to the uranium (IV) oxyhalides. Questions relating to ionic equilibria and the physical properties of aqueous solutions of these compounds are discussed elsewhere (Chapter XVII).

1. Uranyl Fluoride, UO_2F_2

Uranyl fluoride was first prepared by reaction of hydrofluoric acid and uranium oxide. Berzelius (1824) treated UO_3 with hydrofluoric acid and obtained a white amorphous solid on evaporation. Bolton (1866) prepared solutions of uranyl fluoride by treating U_3O_8 with hydrofluoric acid:

(1) $U_3O_8 + 8\ HF \rightarrow UF_4 + 2UO_2F_2 + 4H_2O$

He was unable to obtain crystalline uranyl fluoride from the solution. Smithells (1883), on repeating the work of Bolton, found that uranyl flouride could be obtained as a bright yellow, soapy substance by evaporation of the aqueous solution; on one occasion a partially crystalline material with a mother-of-pearl luster was obtained. Smithells designated the hydrated, amorphous material, obtained by evaporation of aqueous UO_2F_2 solutions, as the β-form, to distinguish it from the compound which he obtained in a very small yield by heating uranium tetrafluoride in a closed crucible and designated as the α- form. The latter probably is anhydrous UO_2F_2, formed by the reaction:

(2) $2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$

Ditte (1884), erroneously formulated the compound, obtained by ignition of uranium tetrafluoride in a limited supply of air, as UOF_4.

1.1 Preparation of Uranyl Fluoride from Aqueous Solution. Uranyl fluoride has a tendency to form acid and basic salts of ill-defined composition. To prepare pure neutral uranyl fluoride (Montreal 1 , a known weight of oxide (UO_3 or $UO_4 \cdot 2H_2O$) is dissolved in the calculated quantity of hydrofluoric acid, and the solution is then evaporated to dryness. The product is usually found to contain a higher percentage of uranium than calculated for the neutral salt. An amount of hydrofluoric acid equivalent to the excess uranium is now added, with enough water to dissolve the salt, and the resulting product from solution is allowed to crystallize. Crystals obtained in this way appear to be the dihydrate, $UO_2F_2 \cdot 2H_2O$.

Uranyl fluoride is difficult to crystallize, very viscous syrups being formed on concentration. Even if uranyl fluoride dihydrate crystals can be induced to form, separation of the crystals from the mother liquor is usually very difficult. The crystals of uranyl fluoride dihydrate are soft, thin plates, pale yellow and so hygroscopic that it is difficult to dry them. Consequently, solutions are often evaporated to dryness at 150°-200°C without attempting to achieve crystallization. At 200°C products with the combination corresponding to that of the neutral salt and containing less than 0.1 per cent water, can be obtained.

Anhydrous uranyl fluoride has also been prepared by reaction of uranyl acetate with hydrofluoric acid (von Unruh, 1909). The acetate is repeatedly evaporated with hydrofluoric acid in a platinum crucible on a water bath to volatilize acetic acid. The residue is then evaporated to dryness to remove water and excess hydrofluoric acid. On prolonged drying in a vacuum desiccator, an anhydrous product is obtained. British workers used this method to prepare UO_2F_2 (British 1).

1.2 <u>Preparation of UO_2F_2 by High Temperature Hydrofluorination</u>. Anhydrous uranyl fluoride is readily prepared by reaction of uranium oxide with HF vapor:

(3) $UO_3 + 2HF \longrightarrow UO_2F_2 + H_2O$

A temperature of 350°-500°C appears suitable (MP Chicago 1). On a comerical scale temperatures as high as 550°C have been recommended (Du Pont 1). Other workers prefer temperatures in the vicinity of 400°C (British 2) (SAM-Columbia 1) to avoid formation of U_3O_8 from the UO_3 and consequent contamination of the product with uranium tetrafluoride. The type of UO_3 used (cf. p.   ) will determine the optimum temperature. This is probably the most convenient method for preparing anhydrous uranyl fluoride.

Although not of particular preparative value, the following reaction can be mentioned as also yielding anhydrous uranyl fluoride:

(4) $UO_2 \cdot HPO_4 \cdot x\ H_2O + 2HF \xrightarrow{350^\circ - 500^\circ C} UO_2F_2 + H_3PO_4 + x\ H_2O$

Above 500°C reduction occurs and uranium tetrafluoride begins to form (CEW-TEC 1).

Uranyl fluoride can be readily prepared by the reaction of anhydrous uranyl chloride with liquid anhydrous hydrogen fluoride at room temperature (Brown 1). The reaction is best carried out in a platinum-lined nickel reactor; the reaction mixture is allowed to stand overnight and the hydrogen chloride and fluoride removed by distillation in vacuum at 450°C. A completely water-soluble, chlorine-free product results.

(a) Miscellaneous Reactions Yielding Uranyl Fluoride as a Product. While not especially desirable as methods of preparation, the following reactions give uranyl fluoride as a product (MP Chicago 1):

(5) $UO_3 + 2F_2 \xrightarrow{350^\circ C} UO_2F_2 + OF_2$ (?)

(6) $UO_2 + F_2 \xrightarrow{350^\circ C} UO_2F_2$

(7) $U_3O_8 + 5F_2 \xrightarrow{350^\circ C} 3UO_2F_2 + 2\ OF_2$ (?)

Uranyl fluoride is one of the products of the reaction (MP Chicago 2):

(8) $2UF_4 + O_2 \longrightarrow UF_6\uparrow + UO_2F_2$

When uranium hexafluoride is treated with water vapor, it has been reported that a complex compound of uranyl fluoride, hydrogen fluoride and water results, from which uranyl fluoride can be prepared by heating to 180°C (British 3). The existence of this complex requires confirmation.

1.3 Physical Properties of Uranyl Fluoride.

(a) Crystal Structures of Anhydrous Uranyl Fluoride. The crystal structure of UO_2F_2 has been studied by Zachariasen (MP Chicago 3). The compound has hexagonal symmetry and forms a layer lattice structure with stacking disorder. The lattice constants are:

$$a_1 = 4.198 \pm 0.002A, \qquad a_3 = 5.228 \pm 0.003A$$

The layers are all identical, and are at a distance a_3 apart. The structure in any one layer is:

1 U at (0,0,0), 2 0 at (0,0,u), with u = 0.37

2 F at ± (1/3,2/3,v), with v = 0.10

The next layer has the same structure, but is displaced either

$1/3\ \underline{a}_1 + 2/3\ \underline{a}_2 + \underline{a}_3$ or $2/3\ \underline{a}_1 + 1/3\ \underline{a}_2 + \underline{a}_3$,

the two possible displacements being equally probable. Due to the stacking disorder, the mean structure corresponds to a unit cell with dimensions $a_1/\sqrt{3}$ and a_3, and the unit cell thus contains only one-third of a molecule.

The density as computed from the x-ray data is 6.37 g/cc. A direct measurement by displacement in benzene gave 5.8 g/cc, but this value was thought to be low due to entrapped air (SAM-Columbia 2). British workers report a pouring density of 2.95 g/cc and a packing density of 2.55 g/cc (British 2).

(b) Optical and Photochemical Properties of Uranyl Fluoride. The absorption and fluorescence spectra of uranyl fluoride will be discussed in the second half of this treatise (Chapter). Anhydrous uranyl fluoride is a pale yellow solid, no other physical constants have been determined. Since uranyl fluoride undergoes thermal decomposition, the melting point is unknown. No thermodynamic data other than those pertaining to the properties of aqueous solutions are available, and these are discussed in Chapter XVII.

1.4 Chemical Properties of Uranyl Fluoride. (a) Water. Anhydrous uranyl fluoride is soluble in water, methanol and ethanol; unlike the other uranyl halides, it is insoluble in ether or amyl alcohol (von Unruh, 1909). The solubility in water has been studied at various temperatures (SAM-Columbia 2). (Table 1)

TABLE 1

SOLUBILITY OF URANYL FLUORIDE IN WATER

t°C	Weight % UO_2F_2	Molality	ρ g/cc
25.0	67.3	5.18	2.405
75.0	69.6	5.59	2.472
99.9	72.4	6.08	2.588

The solubility of uranyl fluoride has also been determined at the SAM-Carbide and Carbon Laboratory. Their data is given in Table 2 (SAM-Carbon and Carbide 1).

TABLE 2

SOLUBILITY OF URANYL FLUORIDE AT VARIOUS TEMPERATURES

t°C	% UO_2F_2	Mole Fraction UO_2F_2
1	61.4	0.0862
25	65.6	0.100
60	71.0	0.125
100	74.1	0.143

By plotting the mole fraction of uranyl fluoride versus the reciprocal of the absolute temperature, the heat of the reaction

(9) $UO_2F_2 \cdot H_2O_{(s)} + H_2O \longrightarrow UO_2F_2$ (saturated solution)

is found to be 1.0 kcal/mole. The solubility of uranyl fluoride in water increases with temperature, but that of uranyl fluoride in hydrofluoric acid has a negative temperature coefficient so that crystallization of uranyl fluoride occurs on heating.

Uranyl fluoride prepared at low temperatures is very hygroscopic, but uranyl fluoride obtained by high temperature hydrofluorination exhibits no deliquesence even on long standing in air. Hydrated uranyl fluoride can be dehydrated at 120°C without serious decomposition (British 2)(SAM-Columbia 3). Hydrates of uranyl fluoride generally appear to be unstable above 100°C. Uranyl fluoride containing an excess of UO_3 requires higher temperatures for complete dehydration (up to 250°C). At 250°C, uranyl fluoride undergoes a color change; it becomes pink, but does not appear to be changed chemically (Montreal 1).

Aqueous solutions of neutral uranyl fluoride do not attack glass even at the boiling point. Solutions of 2 M uranyl fluoride have been heated in pyrex tubes to 200°C for ten days without formation of any precipitate (Montreal 1). Superheated steam at 900°C removes all of the fluorine leaving a residue of U_3O_8. At 450°C the residue is largely UO_3 (MP Ames 1).

(b) <u>The System UO_2F_2-HF-H_2O</u> (SAM-Carbide and Carbon 1). A phase study of this system has been made by the solubility method. (The uranyl fluoride used was prepared by reaction of UO_3 with hydrogen fluoride.) The various mixtures were allowed to come to equilibrium at 25°C in two to three weeks time. The results obtained are presented in Table 3.

The data indicate a marked decrease in solubility with increasing concentration of hydrofluoric acid. In the region investigated only one solid phase appears. On extrapolating the tie lines joining points corresponding

TABLE 3

COMPOSITION OF THE LIQUID AND SOLID PHASES IN EQUILIBRIUM IN THE SYSTEM UO_2F_2-HF-H_2O at 25°C

Liquid Phase				Solid Phase		
% HF	% UO_2F_2	% H_2O	Density $\frac{25^\circ}{25^\circ}$	% HF	% UO_2F_2	% H_2O
0.00	65.55	34.45	2.224	--	--	--
11.88	31.88	56.24	1.440	8.52	51.95	39.53
20.70	22.99	57.01	--	18.20	32.50	49.30
25.75	18.19	56.01	--	14.51	51.25	34.24
32.51	1.35	56.14	1.231	12.06	64.47	23.47
				3.50*	83.76*	12.74*
41.70	6.10	52.20	--	8.77	75.2	16.03

*Partially Dried.

to the compositions of the solution phases and the equilibrium solids, the composition of the equilibrium solid phase is found to be $UO_2F_2 \cdot H_2O$ (Fig. 1).

(c) Thermal Decomposition of Uranyl Fluoride. The compound appears to be stable in air to 300°C. Above 300°C decomposition to U_3O_8 occurs (CEW-TEC 2)(British 4). The thermal decomposition has been studied in some detail at Ames (MP Ames 2). Some decomposition is found to occur even at 200°C, but most of it occurs at 850°-900°C (in vacuum). The substance does not melt. A black coke-like residue of U_3O_8 remains in the furnace; a yellow substance (UO_2F_2(?)) and a green substance (impure UF_4)distill out of the furnace. There is also evidence for the evolution of fluorine (or perhaps UF_6), since

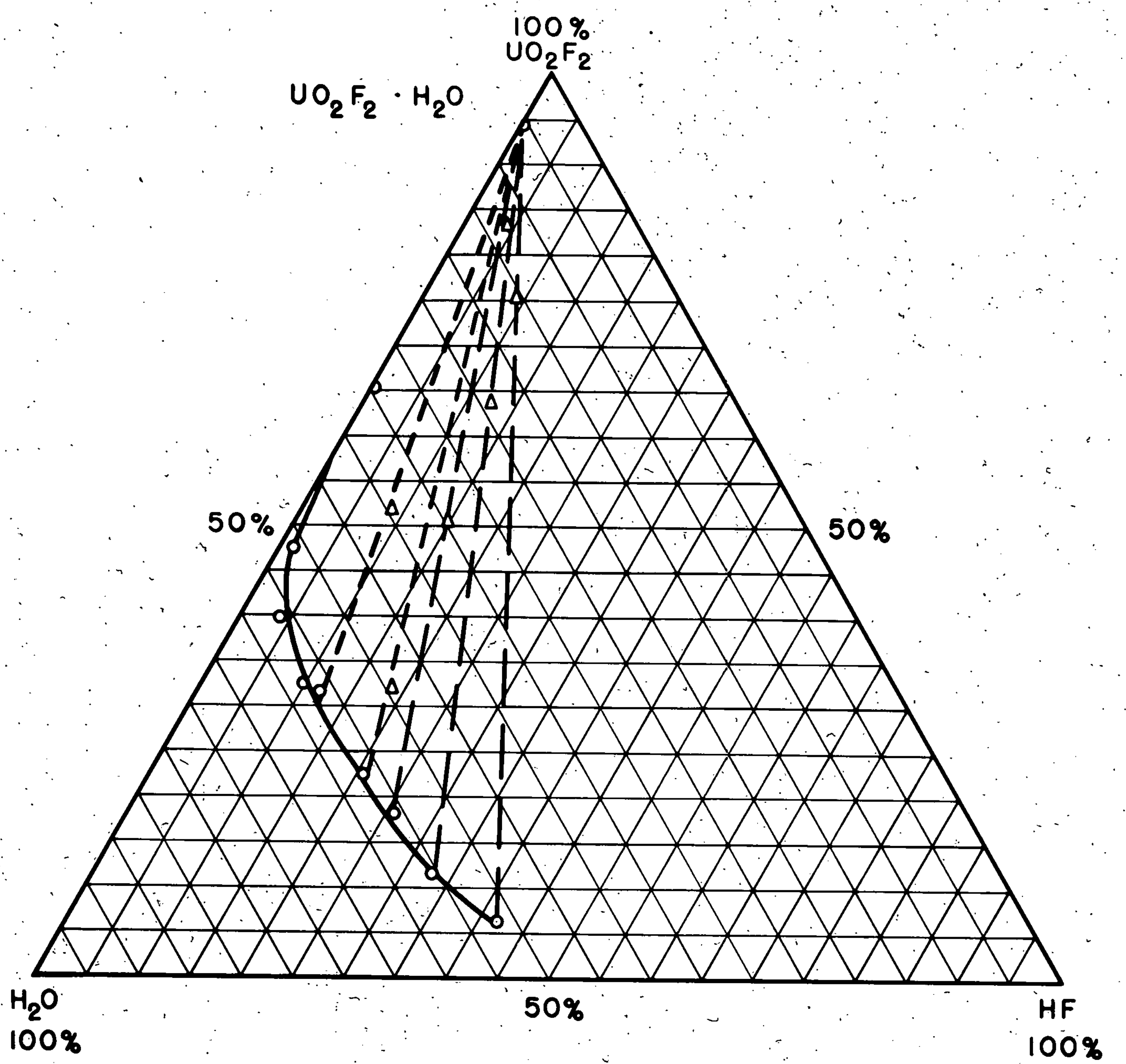

FIG. I. THE URANYL FLUORIDE – HYDROGEN FLUORIDE – WATER SYSTEM AT 25°C.

a deposit of mercurous fluoride is usually found in the mercury vapor pump. The Ames workers postulated a number of concurrent reactions to account for the observed products of thermal decomposition:

(10) $2UO_2F_2 \longrightarrow UO_2 + UF_4 + O_2$

(11) $UO_2F_2 \longrightarrow UO_2 + F_2$

(12) $4UO_2F_2 \longrightarrow U_3O_8 + UF_4 + 2F_2$

The evidence is still too meager to draw any definite conclusions as to the predominant reaction. A primary reaction which could perhaps account for the observed result (at least in part) is:

(13) $3UO_2F_2 \longrightarrow UF_6 + 2/3\ U_3O_8 + 1/3\ O_2$

Davidson and Fried have estimated the ΔF of this reaction; from their computations it appears that a temperature of at least 1300°K would be necessary for it to proceed (MP Chicago 2). Moreover, a number of arbitrary assumptions were involved in computing the free energy of reaction (13), and the possibility that UF_6 actually is formed according to this equation (13) need not be excluded. More work is desirable since formation of UF_6 by decomposition of uranyl fluoride would have some interest.

(d) <u>Some Chemical Reactions of Uranyl Fluoride</u>. Uranyl fluoride undergoes reduction with <u>hydrogen</u>:

(14) $UO_2F_2 + H_2 \longrightarrow UO_2 + 2HF$

This reaction proceeds rapidly at 600°C, rather slowly at 500°C (MP Chicago 1) (DuPont 2). The uranium dioxide so produced is very reactive. Fluorine converts uranyl fluoride to UF_6:

(15) $UO_2F_2 + 4F_2 \longrightarrow UF_6 + 2F_2O$

A temperature of 290°-350°C is suitable (SAM-Columbia 4)(MP Chicago 1). This reaction is especially convenient for the preparation of UF_6.

A reaction, which is typical of all solutions containing UO_2^{++} but which has been applied particularly to uranyl fluoride, is reduction with <u>stannous chloride</u>:

(16) $UO_2F_2 + 4HF + SnCl_2 \longrightarrow UF_4 + Sn\ Cl_2F_2 + 2H_2O$

(For references, see Preparation of Uranium Tetrafluoride, Chapter XII, Section 2).

Solutions of uranyl fluoride containing <u>glucose</u> or <u>alcohol</u> are reduced by direct sunlight to uranium tetrafluoride. Fusion with <u>alkali</u> (NaOH,CaO) converts uranyl fluoride to a mixture of sodium (or calcium) uranate and sodium fluoride or calcium fluoride (Aloy and Rodier, 1922).

(e) <u>Complex salts of Uranyl Fluoride</u>. Uranyl fluoride is coordinatively unsaturated and forms extensive series of double salts. Double salts of the following types are formed with metal fluorides:

A. $M\ UO_2F_3$ or $MF{:}UO_2F_2$ (M=Na)
B. $M_3UO_2F_5$ or $3MF{:}UO_2F_2$(M=K, NH_4, ½Ba)
C. $M_3\ (UO_2)_2F_7$, or $3MF{:}2UO_2F_2$(M=K)
D. $M_5\ (UO_2)_2F_9$ or $5MF{:}2UO_2F_2$ (M=K)

Ditte (1884) described compounds of the series $M_4UO_2F_6$(M=Li, Na, K, Rb, Tl), which he obtained by fusion of U_3O_8 and potassium fluoride with a small amount of carbonate; and also compounds of the type $M_4UOF_8.n\ H_2O$ (M=K, Rb). These latter have been shown by Smithells to be in all probability of Type B, whereas the former were simply uranates (Smithells, 1883). Recently, the preparation of the two compounds, $Cs_4UO_2F_6$ and $K_4UO_2F_6$, has been reported (SAM-Columbia 5), but no details of preparation or analysis were given. The cesium compound forms monoclinic prismatic crystals. Since there does not appear to be any obvious reason why complex compounds of the type $4MF.UO_2F_2$ should not exist, they may well be obtainable although probably not by the methods of Ditte.

Although the UO_2F_2 complexes were discovered and studied by Bolton (1886), it was Baker (1879) who first elucidated their relationships. When potassium fluoride is added to a solution of uranyl nitrate or uranyl fluoride, $K_3UO_2F_5$ precipitates. If this salt is recrystallized from pure water (or an aqueous solution containing less than 13 per cent KHF_2), $K_5(UO_2)_2F_9$ is formed. Further if either $K_3UO_2F_5$ or $K_5(UO_2)_2F_9$ is recrystallized from uranyl nitrate solution, $K_3(UO_2)_2F_7$ is formed.

Of these salts, $\underline{K_3UO_2F_5}$ has been studied in some detail. It melts at red heat with decomposition. On heating in air, fluorine is lost and the compound is converted to uranate. The salt is completely decomposed by warm concentrated sulfuric acid. Ammonia or sodium hydroxide precipitate diuranates, but ammonium and sodium carbonates yield water soluble complexes. This reaction indicates that the uranium is not held in a very tight complex. A solution of $K_3UO_2F_5$ gives no precipitate with copper, silver, zinc, mercury, iron, or platinum salts; but barium, calcium, and lead ions precipitate insoluble complex salts of the type $Ba_3(UO_2)_2F_{10}\cdot 2H_2O$. Photoreduction of an oxalic or formic acid solution of $K_3UO_2F_5$ results in precipitation of K_2UF_6. All of the complex salts undergo conversion to uranates on heating in air or on fusion with sodium carbonate; the ammonium salt is of course converted to U_3O_8 on ignition with loss of ammonium fluoride.

Hydrogen peroxide oxidizes aqueous solutions of $NaUO_2F_3$ or $K_3UO_2F_5$ to insoluble per-compounds which have been formulated as $NaUO_4F\cdot 5H_2O$ and

$K_4U_4O_{15}F_6 \cdot 4H_2O$. These formulas cannot be considered as firmly established. The per-compounds decompose above 100°C with evolution of oxygen (Lordkipanidse, 1900). The conductivity of aqueous solutions of $K_3UO_2F_5$ and $(NH_4)_3UO_2F_5$ have been studied (Miolati and Alvisi, 1897), and the results purport to show the existence of stable $(UO_2F_5)^{\equiv}$ ions (compare with crystallographic evidence below). Table 4 summarizes some pertinent data on the preparation and crystallographic properties of these complex salts.

The crystal structure of $K_3UO_2F_5$ has been studied recently (MP Chicago 4). Material prepared by addition of potassium fluoride to a concentrated uranyl nitrate solution was found to consist of a single phase, anhydrous $K_3UO_2F_5$. The compound has a tetragonal structure with a body centered translation group. The unit cell with the dimensions $a_1 = 9.05 \pm 0.05A$, $a_3 = 18.10 \pm 0.10A$, contains eight molecules. The calculated density is 4.29 g/cc and the probable space group is I4/amd. An approximate structure has been deduced; an interesting feature is the existence of $[UO_2F_4]^{=}$ -units in the lattice with the fifth fluorine bound only to potassium.

Uranyl fluoride forms a series of addition compounds with <u>ammonia</u> (Von Unruh, 1909). Liquid ammonia reacts with uranyl fluoride (or lower ammoniated complexes) to give $UO_2F_2 \cdot 4NH_3$, a deep orange red substance which is more stable than the corresponding derivatives of uranyl bromide and uranyl chloride. Gaseous ammonia reacts with uranyl fluoride to give $UO_2F_2 \cdot 3NH_3$ (orange-yellow) which on warming is converted to $UO_2F_2 \cdot 2NH_3$ (yellow).

TABLE 4

PREPARATION AND PROPERTIES OF COMPLEX COMPOUNDS OF URANYL FLUORIDE AND METAL FLUORIDES

Compound	Ratio of Metal Fluoride to UO_2F_2	Crystal Habit (1)	Crystallographic Data (1)	Density (1) g/cc 20°C	Solubility	Preparation
$NaUO_2F_3 \cdot 4H_2O$	1:1	Monoclinic	a:b:c: = 1.0270:1:0.5222 β= 94°51'			Crystallizes by slow evaporation of a solution of uranyl nitrate and NaF, or a solution of sodium uranate in HF. Exact conditions are unknown. The dihydrate is obtained on recrystallization from H_2O (2)
$K_3UO_2F_5$	3:1	Tetragonal. No appreciable fluorescence.	a:c = 0.992	4.263	12.5g/100g H_2O at 21°C (2) Precipitates by addition of alcohol.	Ppts. as a yellow crystalline solid on addition of a slight excess of KF to $UO_2(NO_3)_2$ soln. This is the primary reaction product of KF and UO_2F_2 or $UO_2(NO_3)_2$ solutions (1)(2)(3)
$(NH_4)_3UO_2F_5$	3:1	Tetragonal. Strongly fluorescence in x-ray or ultraviolet light.	Refractive index = 1.495 (5)	3.186	10.11g/100g soln. at 27°C. 20.70g/100g soln. at 81.3°C (4) Insol. in C_2H_5OH	Addition of $(NH_4F$ to a solution of uranyl nitrate (2)(1)

TABLE 4

PREPARATION AND PROPERTIES OF COMPLEX COMPOUNDS OF URANYL FLUORIDE AND METAL FLUORIDES

Compound	Ratio of Metal Fluoride to UO_2F_2	Crystal Habit(1)	Crystallographic Data(1)	Density(1) g/cc 20°C	Solubility	Preparation
$Ba_3(UO_2)_2F_{10}\cdot 2H_2O$	3:1				Very sparingly sol. in hot water	$BaCl_2$ + $K_3UO_2F_5$ solution. The dihydrate is obtained by drying at 100°C. Ca and Pb compounds are obtained in the same way.(2)
$K_3(UO_2)_2F_7\cdot 2H_2O$	3:2	Monoclinic. Distinct green fluorescence	a:b:c =0.918:1:0.978 β = 114°0	4.108	Sol. in warm water	Prepared by addition to a solution of UO_2F_2 of an amount of KF insufficient to cause a permanent precipitate and then evaporating or, by crystallizing $K_3UO_2F_5$ or $K_5(UO_2)_2F_9$ from $UO_2(NO_3)_2$ or UO_2F_2 solution.(1)
$K_5(UO_2)_2F_9$	5:2	Triclinic. Large crystals show distinct fluorescence	a:b:c=0.6222:1:0.568 α = 72°38' β = 116°23' γ = 111°57'	4.379		Prepared by recrystallization of $K_3UO_2F_5$ from water or from a less than 13 % KHF_2 solution.(1)

(1) (Baker, 1879)
(2) (Bolton, 1866)
(3) (Smithells, 1883)
(4) (Bürger, 1904)
(5) (Bolland, 1910)

Complex compounds with organic bases have also been prepared (Olsson, 1930). A solution of the appropriate base (in dilute hydrofluoric acid) is added to a solution of uranyl nitrate (containing F^-). The precipitate is removed, washed first with dilute hydrofluoric acid, then with water, and finally dried on filter paper. Most compounds are stable in air for long periods; heat converts them to U_3O_8. They are somewhat soluble in water, and the solubility usually increases as the temperature is raised. The complexes dissolve in acids; bases, such as sodium hydroxide or ammonia precipitate uranates. Carbonates form soluble complexes. No solubility is observed in organic solvents, such as glacial acetic acid, alcohol, ether, or acetone. Table 5 lists a number of these compounds and their solubilities in water.

The compounds are of three types:

I	$MUO_2F_3 \cdot nH_2O$	or	$MF \cdot UO_2F_2$	where M is an univalent organic base
II	$M(UO_2)_2F_5 \cdot nH_2O$	or	$MF \cdot 2UO_2F_2$	
III	$M(UO_2)_3F_7 \cdot nH_2O$	or	$MF \cdot 3UO_2F_2$	

2. Uranium (IV) Oxyfluoride, UOF_2

Preparation of the compound $UOF_2 \cdot 2H_2O$ has been claimed by Giolitti and Agamennone (1905). Giolitti (1904) had developed an analytical method for uranium based on the precipitation of uranium tetrafluoride. The results he obtained by this procedure were very erratic, and in seeking the reason for this he came to the rather surprising conclusion that uranium tetrafluoride does not exist at all, and that uranium oxyfluoride, is the compound which precipitates when hydrofluoric acid is added to a U(IV) solution.

TABLE 5
COMPLEX COMPOUNDS OF URANYL FLUORIDE WITH ORGANIC BASES

Base	Compound	Solubility g/100 cc H_2O at 20°C
Pyridonium	$C_5H_6NHUO_2F_3\cdot H_2O$	1.289
Pyridonium	$C_5H_6NH(UO_2)_2F_5\cdot 3H_2O$	1.952
Quinolonium	$C_9H_8NHUO_2F_3\cdot H_2O$	0.126
Quinolonium	$C_9H_8NHUO_2F_5\cdot 2H_2O$	0.979
Tetramethylammonium	$(CH_3)_4N(UO_2)_2F_5\cdot 2H_2O$	0.143
Tetraethylammonium	$(C_2N_5)_4NUO_2F_3$	0.716
Tetraethylammonium	$(C_2H_5)_4NUO_2F_3\cdot 2H_2O$	0.771
Trimethyl-p-tolyl ammonium	$(CH_3C_6H_4)(CH_3)_3NUO_2F_3\cdot 2H_2O$	1.645
Trimethyl-p-tolyl ammonium	$(CH_3C_6H_4)(CH_3)_3N(UO_2)_2F_5\cdot H_2O$	3.091
Tetramethyl pyridonium	$(C_5H_2)(C\ H_3)_4NH(UO_2)_3F_7\cdot 6H_2O$	0.708
Diethyl anilonium	$C_6H_5N(C_2H_5)_2HUO_2F_5\cdot 2H_2O$	1.759
Diethyl anilonium	$C_6H_5N(C_2H_5)_2H(UO_2)_2F_5\cdot 2H_2O$	3.896
Triethyl sulfonium	$(C_2H_5)_3S(UO_2)_2F_5\cdot 2H_2O$	0.897
Trimethylammonium	$(CH_3)_3NH(UO_2)_2F_5\cdot 2H_2O$	
Propyl ammonium	$C_3H_7NH_3UO_2F_5\cdot 2H_2O$	
Propyl ammonium	$C_3H_7NH_3(UO_2)_3F_7\cdot 6H_2O$	
Tetrapropyl ammonium	$(C_3H_7)_4N(UO_2)_3F_7\cdot 2H_2O$	
Methyl ethyl propyl phenyl ammonium	$(CH_3)(C_2H_5)(C_3H_7)(C_6H_5)N\cdot(UO_2)_3F_7\cdot 6H_2O$	
Anilonium	$C_6H_5NH_3UO_2F_3\cdot 3H_2O$	
Dimethyl anilonium	$C_6H_5N(CH_3)_2H(UO_2)_2F_5\cdot H_2O$	

There can be little doubt that Giolitti's conclusions were based on very inadequate analytical methods. The fluorine determinations could easily have been in error by several hundred per cent.

In the course of this work, Giolitti and Agamennone made several observations of the reaction of hydrofluoric acid and U_3O_8, which have been confirmed by more recent investigators (MP Ames 3)(MP Chicago 5). When U_3O_8 is treated with hydrofluoric acid, two solid phases appear which can be readily separated by flotation because of the difference in density. The less dense material is blue-green, the more dense, green. The nature of these two phases is still in doubt.

The Brown University Group attempted to prepare uranium(IV) oxyfluoride by treating uranium(IV) oxychloride with liquid anhydrous hydrogen fluoride at room temperature, but uranium tetrafluoride was the only product obtained (Brown 1).

3. Uranyl Chloride, UO_2Cl_2

Anhydrous uranyl chloride can be prepared only by high temperature, vapor phase reactions. Although aqueous solutions of uranyl chloride can be readily obtained, they have not as yet been dehydrated without formation of basic salts.

3.1 Preparation of Anhydrous Uranyl Chloride. The reaction

(17) $UO_2 + Cl_2 \rightarrow UO_2Cl_2$

was employed by Peligot (1842) to prepare anhydrous uranyl chloride. The reaction is carried out at red heat with dry chlorine. It is usually incomplete, and Regelsberger (1885) employed ether extraction to separate the uranyl chloride from the unreacted oxide. Unfortunately, the ether cannot then be completely removed. The Brown University Group found that the reaction between UO_2 and commercial dry chlorine proceeds at 500°C, to give a product containing some U_3O_8 (Brown 2). With UO_3, chlorine does not react at 400°C; above 400°C U_3O_8 is formed (MP Ames 4). Active UO_2, prepared by reduction of UO_3 with methane, (cf. p), was reported to yield uranyl chloride on treatment with chlorine (UCRL 1). With $U_3O_2S_2(UO_2 \cdot 2US)$ and chlorine, reaction occurs at 60°C. After it is over, the UCl_4 formed can be sublimed away in a stream of chlorine at 600°C, leaving a residue of yellow, anhydrous uranyl chloride (MP Ames 5).

A number of other reactions are known in which anhydrous uranyl chloride is formed. When carbon tetrachloride reacts with various uranium oxides, some uranyl chloride is formed which presumably could be separated from concurrently produced uranium tetrachloride either by vacuum sublimation at elevated temperatures, of by sublimation in a stream of chlorine (see Chapter XIV). Thus, when UO_3 is treated with carbon tetrachloride vapor at 290°C, a product containing 23 per cent UO_2Cl_2 and 77 per cent UCl_4 is obtained (UCRL 2). If carbon monoxide or, better, chloroform is introduced with the carbon tetrachloride, the yield of uranyl chloride is increased. (UCRL 3) However , these are not particularly convenient preparative reactions.

Hydrogen chloride reacts readily with uranium trioxide to form uranyl chloride. The reaction is exothermic and proceeds spontaneously at room temperature. Moisture must be present, for if anhydrous UO_3 is used, the reaction is extremely slow. A closed system, containing partially hydrated UO_3 is evacuated without heating to remove air but leave as much water as possible. Hydrogen chloride is then introduced at a rate sufficient to maintain a pressure of one atmosphere in the reaction system. Some eighteen to twenty-four hours at room temperature are required for completion of the reaction. Material so prepared has the formula $UO_2Cl_2 \cdot H_2O$. The hydrated uranyl chloride can be dried without decomposition in a current of dry hydrogen chloride gas at 300°C (Brown 3). It has been reported (without detail) that UO_3 suspended in ethanol or carbon tetrachloride gives uranyl chloride on treatment with hydrogen chloride (Purdue 1). The preparative value of this reaction is unknown.

Probably the best method for the preparation of anhydrous uranyl chloride is the reaction of uranium tetrachloride with oxygen at 300-350°C:

(18) $$UCl_4 + O_2 \rightarrow UO_2Cl_2 + Cl_2$$

There is a tendency for the reaction mass to sinter preventing complete conversion; it can be counteracted by agitating the reaction tube. Mixtures of UCl_5 and UCl_6 and UCl_3 also react with oxygen to give uranyl chloride, but UCl_4 appears to be the best starting material (MP Ames 4).

Acetyl chloride, CH_3COCl, reacts with various oxides to give halides or oxyhalides (Chretien and Oechsel, 1938). With UO_3 and liquid CH_3COCl at room temperature, one obtains $UO_2Cl_2 \cdot (CH_3CO)_2O$, a pale-yellow crystalline powder. Whether pure uranyl chloride could be obtained from this complex is not stated. Further work would be interesting.

3.2 <u>Preparation of Uranyl Chloride Hydrates</u>. Aqueous solutions of uranyl chloride have been prepared by careful oxidation of a solution of uranium tetrachloride with nitric acid (Arfvedson, 1824), by solution of $UO_3 \cdot H_2O$ in an equivalent amount of hydrochloric acid (Mylius and Dietz, 1901), and also by the addition of the stoichiometric amount of barium chloride to a solution of uranyl sulfate (de Coninck, 1909). Solid hydrates can be prepared by evaporation from such solutions. Usually, amorphous products are obtained, but slow evaporation in a desiccator yields yellowish-green, doubly refracting, fluorescent, easily decomposed crystals of $UO_2Cl_2 \cdot 3H_2O$ (Mylius and Dietz, 1901). Crystallization can sometime be induced by introducing into a concentrated solution of uranyl chloride a few seed crystals, prepared by treating some of the semi-amorphous material with concentrated hydrochloric acid and allowing it to crystallize spontaneously by slow evaporation in a desiccator.

The monohydrate $UO_2Cl_2 \cdot H_2O$ has been reported (de Coninck, 1909) to be formed by slow evaporation of an aqueous solution in dry air. Evaporation of a uranyl chloride solution at 120°C to dryness has also been stated to yield $UO_2Cl_2.H_2O$ (SAM-Columbia 6). Saturation with hydrogen chloride of a saturated aqueous solution of uranyl chloride at -10°C gives $UO_2Cl_2 \cdot HCl \cdot 2H_2O$ as yellow, very unstable crystals (Aloy, 1901).

All of the above-mentioned workers were of the opinion that hydrated uranyl chloride could not be dehydrated without serious decomposition. Mylius and Dietz reported that hydrogen chloride is evolved even at room temperature when evaporation is attempted. The tendency to form basic salts is great. A compound, $UO_2(OH)Cl \cdot 2H_2O$ has been isolated in the form of small yellow needles (Mylius and Dietz, 1901), from the sirupy evaporation product of a uranyl chloride solution. This substance is probably identical with that described much earlier by Lecanu (1825). It is more stable than uranyl chloride hydrate; the water of crystallization is lost at 150°C without further decomposition.

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3.3 Physical Properties of Uranyl Chloride.

(a) Crystal Structure (MP Ames 6). X-ray diagrams have been obtained for anhydrous uranyl chloride powder and for the needles obtained by condensing uranyl chloride from the vapor (500°C). The two forms are different, as the needles show many maxima which are absent from the powder diagram. The crystal is orthorhombic with four moleclues per unit cell. The lattice constants are:

Needles: $a_o = 8.71 \pm 0.01A$, $b_o = 8.39 \pm 0.01A$, $c_o = 5.72 \pm 0.01A$

Powder: $a_o = 8.69 \pm 0.01A$, $b_o = 8.39 \pm 0.01A$, $c_o = 5.70 \pm 0.01A$

The density calculated from the x-ray data is 5.426 g/cc. A direct measurement of the density by benzene displacement gave 5.28 g/cc (MP Ames 5).

(b) Volatility. Uranyl chloride was described as somewhat volatile in a stream of chlorine or oxygen above 500°C. It has been found, however, that uranyl chloride will not markedly volatilize at 630°C in a chlorine atmosphere, in seven hours (Purdue 2). The volatility has been studied by tracer techniques with results which indicated no substantial volatility below 775°C. These results require confirmation (Berkeley 1). Decomposition renders interpretation of the volatility data difficult. Anhydrous uranyl chloride has been reported to melt at a relatively low temperature (red heat). The vapor was reported to be orange-yellow in color (Peligot, 1842).

(c) Miscellaneous. Crystals of anhydrous uranyl chloride show no triboluminescence (Trautz, 1905) . Molten uranyl chloride conducts an electric current; chlorine is evolved and uranium dioxide separates out of the melt (Hampe, 1888).

3.4 Chemical Properties of Uranyl Chloride. Anhydrous uranyl chloride is a bright-yellow crystalline substance. The hydrates have a greenish cast and appear to be fluorescent. Both anhydrous and hydrated uranyl chloride are very hygroscopic and rapidly form viscous solutions on exposure to air. In dry air the compounds are stable indefinitely.

(a) Solubility in Water and the Stability of Aqueous Solutions. Uranyl chloride, its hydrates and basic salts are all very soluble in water. The trihydrate is soluble to the extent of 746 parts per 100 parts of water at 18°C, and even more at higher temperatures (Mylius and Dietz, 1901), but this seems strange. The solubility is reported to be higher in hydrochloric acid solution (Aloy, 1901a). The density of the saturated aqueous solution at 18°C is 2.740 g/cc, which is sufficiently high to float glass or quartz. The density of solutions between 1 and 10 per cent uranyl chloride at 13-16°C lies between 1.0056 and 1.0517 g/cc (de Coninck, 1904). The molar heat of solution of $UO_2Cl_2 \cdot H_2O$ (in 2500 mole H_2O) has been determined as 6.05 kcal (at 18°-20°C) (Aloy, 1896). This value is uncertain because of the indefinite composition of the salt.

Aqueous solutions of uranyl chloride are thermally and photochemically unstable (Mylius and Dietz, 1901). Solutions are usually acid to litmus, indicating appreciable hydrolysis. Although de Coninck (1909a) was unable to verify the existence of $UO_2(OH)Cl \cdot 2H_2O$ (which has been found by other workers), the formation of such basic salts as a result of hydrolysis seems fairly well established (cf above p.).

(For other details as to the properties of aqueous solutions of uranyl chloride, consult the general discussion in Chapter XVII.).

(b) Non-Aqueous Solutions of Uranyl Chloride. Uranyl chloride is said to dissolve in methyl acetate, ethyl acetate, acetone, and pyridine, but whether reaction occurs is not stated (Naumann, 1904,1909). Anhydrous uranyl chloride is insoluble in carbon tetrachloride, xylene, and benzene. It does not dissolve in, but reacts with, ethers and chloroform. It is soluble in alcohols, acetophenone, pyridine, and dioxane, but reaction occurs with all of these solvents (MP Ames 4). Uranyl chloride trihydrate is soluble in alcohol and ether.

Von Unruh (1909) prepared anhydrous uranyl chloride solutions in amylol by repeated evaporation of uranyl acetate, first with hydrochloric acid then with water, dissolving the hydrated uranyl chloride in amylol, and distilling the water off, with some of the amylol.

(c) Thermal Stability. Uranyl chloride and its hydrates readily undergo decomposition at elevated temperatures. Uranyl chloride is converted to U_3O_8 by ignition in air. The Brown University Group reports that uranyl chloride decomposes in vacuum with evolution of chlorine at temperatures above 450°C, leaving a mixture of UO_2 and U_3O_8 (Brown 4). The thermal stability has been further studied at Ames (MP Ames 5). In a stream of nitrogen decomposition to UO_2 and chlorine occurs above 400°C. In vacuum, it begins at 300°C. In a stream of chlorine uranyl chloride melts to a reddish-brown liquid at about 500°C. As the temperature is increased to 900°C, decomposition to UO_2 and chlorine occurs, with some sublimation of uranyl chloride and of UCl_5 formed by reaction with chlorine. The bulk of the uranyl chloride is converted to black crystalline UO_2. X-ray studies have shown that the UO_2 obtained in this way is slightly different from ordinary brown UO_2.

(d) Reducing Agents. Anhydrous uranyl chloride is reduced to UO_2 and potassium chloride by metallic potassium (Peligot, 1842). Magnesium at red heat partially reduces uranyl chloride to uranium metal (Seubert, and Schmidt, 1892). Hydrogen, zinc, or copper turnings fail to do so (de Coninck, 1904,1909b). Hydrogen sulfide reduces uranyl chloride to UO_2, sulfur and hydrogen chloride.

(e) Alkalis (de Coninck, 1904,1909). Fusion with potassium hydroxide or sodium hydroxide in air gives a mixture of diuranate with a small amount of uranate. With calcium hydroxide, U_3O_8 and some $CaUO_4$ form; if air is excluded, UO_2 is formed instead of U_3O_8. Barium hydroxide acts similarly. Calcium oxide and barium oxide in air give some U_3O_8 and in the case of CaO, also some $CaUO_4$ and $Ca_2U_2O_7$, whereas BaO gives principally $Ba_2U_2O_7$. Strontium hydroxide and strontium oxide behave similarly to the barium compounds.

(f) Acids (de Coninck, 1903,1904). Uranyl chloride evolves chlorine and nitrogen oxides on warming with nitric acid. Concentrated sulfuric acid converts uranyl chloride to uranyl sulfate with evolution of hydrogen chloride. Selenic acid dissolves uranyl chloride; on warming, chlorine is evolved and a solution of uranyl selenite is formed.

(g) Reacts in Aqueous Solutions. Aqueous solutions of uranyl chloride exhibit all the reactions characteristic of the uranyl ion, to be discussed in (Chapter).

(h) Complex Compounds of Uranyl Chloride with Ammonia and Organic Bases. An extensive series of uranyl chloride ammoniates is known.

Vacuum-dried uranyl chloride absorbs two molecules of ammonia to form an orange compound, $UO_2Cl_2.2NH_3$; of the two NH_3 molecules , one is bound so strongly as to be retained in vacuum (Peters, 1909,1912). An ether solution of uranyl chloride, when treated with ammonia, forms a precipitate, $UO_2Cl_2 \cdot 2NH_3 \cdot (C_2H_5)_2O$, from which the ether can be removed in vacuum (Regelsberger, 1885). The same etherate also can be obtained from an amyl alcohol solution of uranyl chloride by treatment with ammonia; and treatment of the dried precipitate with ether (Von Unruh, 1909). The diammoniate is decomposed by warming to 100°C with formation of ammonium chloride; on ignition in air it is converted to U_3O_8. It is reduced at elevated temperatures by hydrogen or ammonia to UO_2 (Regelsberger, 1885). A triammoniate is also known, but only in the form of an etherate, $UO_2Cl_2 \cdot 3NH_3 \cdot (C_2H_5)_2O$ (Regelsberger, 1885). This compound is obtained by treatment of the diammoniate etherate with gaseous ammonia; it is an orange material, stable in air at room temperature, but losing ammonia on heating. An unstable tetraammoniate is formed by treating uranyl chloride with liquid ammonia at 5°C. The orange-red, amorphous solid begins to decompose at 10°C (Von Unruh, 1909). Rosenheim and Jacobsohn (1906) observed the formation of a grey-green precipitate when uranyl chloride was treated with liquid ammonia, but its composition was not established.

The most precise work on the uranyl chloride/ammonia system is that of Spacu (1936), who studied the reaction of liquid ammonia and uranyl chloride at -78°C. Under these conditions uranyl chloride is found to form decaamoninate, $UO_2Cl_2 \cdot 10NH_3$. As the temperature is raised, ammonia is evolved, and vapor pressure measurements have indicated the existence of the complexes $UO_2Cl_2 \cdot 5NH_3$, $UO_2Cl_2 \cdot 4NH_3$, $UO_2Cl_2 \cdot 3NH_3$, $UO_2Cl_2 \cdot 2NH_3$ and $UO_2Cl_2 \cdot NH_3$. Figure 2 illustrates the results from which these conclusions were drawn. The temperatures of the isothermal lines in Figure 2 indicate the thermal stability ranges of the various compounds. The pentaammoniate is particularly unstable, even at -44°C, whereas the monoammoniate is quite stable up to 130°C.

The heat of formation of the ammoniates varies from -9.63 kcal/mole for $UO_2Cl_2 \cdot 5NH_3$ to -18.03 kcal/mole for $UO_2Cl_2 \cdot NH_3$.

A number of organic bases also form complex compounds with uranyl chloride. It appears that while the coordination sphere of uranium in uranyl chloride can accommodate a maximum of four ammonia molecules, steric considerations usually limit the number of organic groups to two. The preparation and properties of a number of such complexes are given in Table 6. The complexing groups include, in addition to basic nitrogen compounds, also compounds the basic properties of which are due to oxygen or sulfur.

(1) Complex Compounds of Uranyl Chloride and Metal Halides. Uranyl chloride forms a series of double salts of the type $M_2UO_2Cl_4$, where M = a univalent metal or equivalent ion. J. Aloy (1901a) prepared anhydrous $K_2UO_2Cl_4$ and $Na_2UO_2Cl_4$ by treating the appropriate alkali halide with uranyl chloride vapors at red heat. The double salts are described as golden yellow water-soluble solids which melt at red heat without evolving any vapors.

Compounds of this type can also be prepared from aqueous solution; in which case the dihydrate is usually obtained. The compounds $K_2UO_2Cl_4 \cdot 2H_2O$

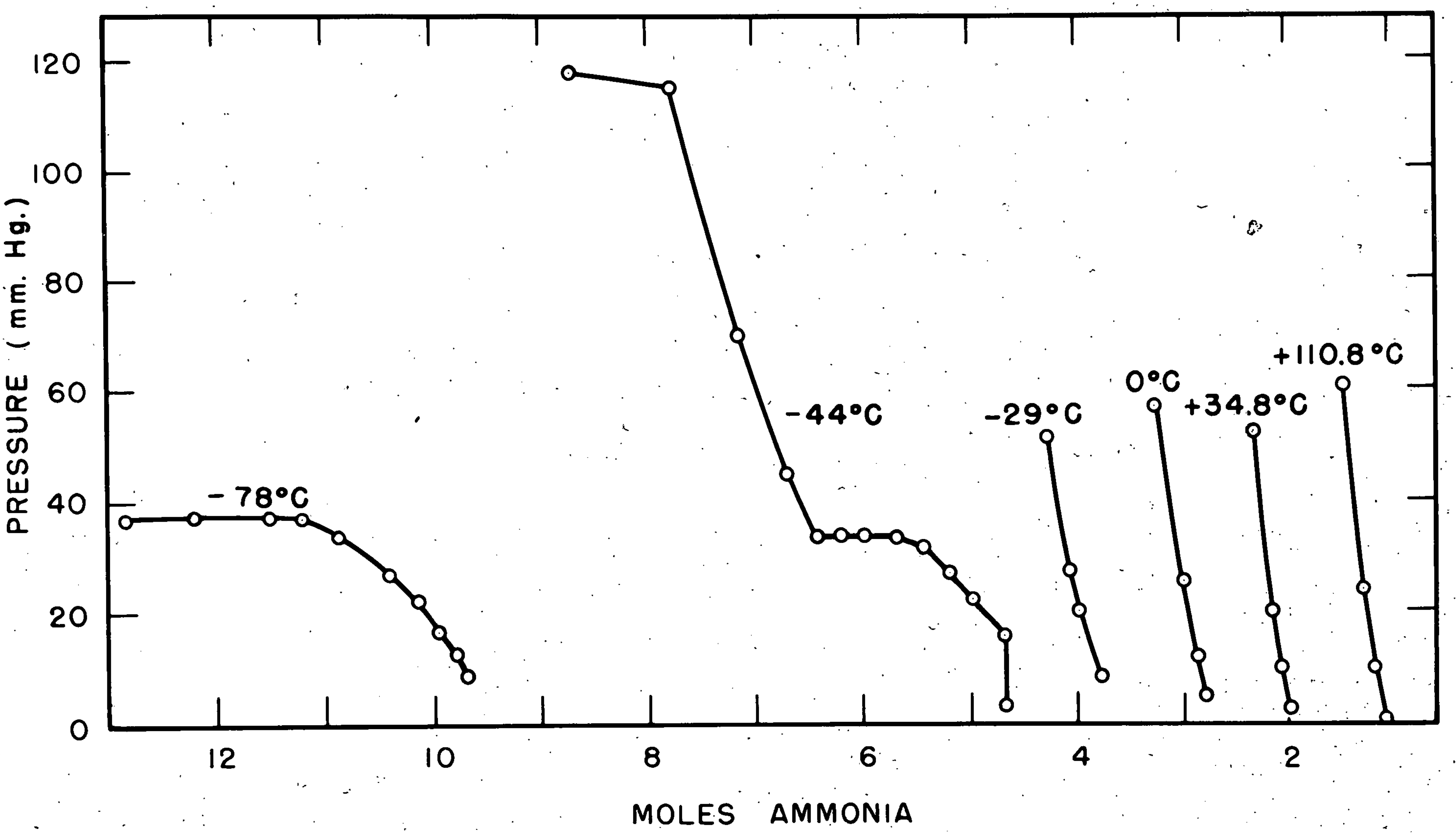

FIG. 2. THE URANYL CHLORIDE-AMMONIA SYSTEM. (FROM P. SPACU, Z. ANORG. ALLGEM. CHEM., 230, 183 (1936)).

TABLE 6

COMPLEX COMPOUNDS OF URANYL CHLORIDE WITH ORGANIC BASES

Organic Base	Complex	Method of Preparation	Properties	Solubility							
				Water	Ethanol	Amyl alcohol	Ether	Ethyl acetate	Acetone	Chloroform	Benzene
Ethyl ether (1)	$UO_2Cl_2\cdot 2(C_2H_5)_2O$	Evapn. of a soln. of UO_2Cl_2 in ether	Yellow needles; decomps. in moist air. Ether cannot be removed.								
2, 3 Dimethyl chromone (2)	$UO_2Cl_2\cdot 2C_{11}H_{10}O_2$	From concd. HCl soln. of components. Recrystd. from concd. HCl.	Long glistening bright yellow prisms. Decomps. without melting.		sl. sol				sl. sol		
2, 3 Dimethyl thiochromone (3)	$UO_2Cl_2\cdot 2C_{11}H_{10}OS$	From concd. HCl soln. of components by evapn.			sl. sol				sl. sol		
Aniline (4)	$UO_2Cl_2\cdot 2C_6H_5NH_2$	From an alcoholic soln. of the components. Recrystn. from alc.	Small yellow needles		sol						
p-Touidine (4)	$UO_2Cl_2\cdot 2C_7H_7NH_2$	Evapn. of alc. soln. of components	Yellow green rhombic crystals.								
Pyridine (5)	$UO_2Cl_2\cdot 2C_5H_5N$	From soln. of $UO_2Cl_2\cdot xH_2O$ in amyl alc. and $CHCl_3$ soln. of pyridine, on cooling.	Yellow, weak green fluorescence. Very hygroscopic.	sol	sol hot		in-sol		in-sol	in-sol	in-sol

TABLE 6 (contd.)

COMPLEX COMPOUNDS OF URANYL CHLORIDE WITH ORGANIC BASES

Organic Base	Complex	Method of Preparation	Properties	Solubility							
				Water	Ethanol	Amyl alcohol	Ether	Ethyl acetate	Acetone	Chloro-form	Benzene
p-Nitroso dimethyl aniline(6)	$UO_2Cl_2 \cdot 2(CH_3)_2NC_6H_4NO$	From a warm alcoholic soln. of the components.	Brick-red Stable in air.	Dif sol		in-sol	sl. sol		in-sol	sl. sol	
p-Nitroso diethyl aniline(7)	$UO_2Cl_2 \cdot 2(C_2H_5)_2NC_6H_4NO$	From warm alcoholic soln. of the components.	Orange-colored Amorphous	dif sol		in-sol	sl sol		in-sol	sl. sol	
Diketopiperazine(8)	$UO_2Cl_2 \cdot C_4H_6N_2O_2 \cdot 1.5H_2O$		Yellow crystals stable in air.								
Acet-p-phenetidine(9)	$UO_2Cl_2 : 2C_{10}H_{13}O_2N$ $UO_2Cl_2 \cdot 3C_{10}H_{13}O_2N$	From a warm alcoholic soln. From warm amyl alcohol soln.	Yellow crystals with green fluorescence stable in air	sol	sol hot	sol hot	V. sl. sol		sol	V. sl. sol	
Methyl acetanilide(10)	$UO_2Cl_2 \cdot 2C_6H_5N(CH_3)COCH_3$	From ethyl or amyl alcohol soln. of components	Shining tabular yellow crystals	sol	sol	sl. sol	sl. sol				
Phenyl dimethyl pyrazolone(11) (Antipyrine)	$UO_2Cl_2 \cdot 2C_{11}H_{12}N_2O$	From an aqueous soln. of the components	Stable in air even on heating	sol	dif sol		sol			sol	

TABLE 6 (contd)
COMPLEX COMPOUNDS OF URANYL CHLORIDE WITH ORGANIC BASES

Organic Base	Complex	Method of Preparation	Properties	Solubility							
				Water	Ethanol	Amyl alcohol	Ether	Ethyl acetate	Acetone	Chloroform	Benzene
Bromo anti-pyrine(12)	$UO_2Cl_2 \cdot 2C_{11}H_{11}BrN_2O$	From alcoholic solns. of the components in the warm.		sol	sol hot		in-sol	V. sl sol	V. sl sol	in-sol	
Dimethylamino-Antipyrine (Pyramidon)(13)	$UO_2Cl_2 \cdot C_{11}H_{11}N(CH_3)_2N_2O$ $UO_2Cl_2 \cdot 2C_{11}H_{11}N(CH_3)_2N_2O$	From alcoholic solns. of components in warm. From alcoholic solns. of components in cold.	Amorphous Yellow	sol	sol	sl. sol	in-sol		sl. sol	sl. sol	

(1)(Regelsberger, 1885).
(2)(Simonis and Elias, 1915).
(3) (Simonis and Elias, 1916).
(4) (Leeds, 1881).
(5) (Rascanu, 1930-1931).
(6) (Rascanu, 1931-1932).
(7) (Rascanu, 1931-1932a).
(8) (Asahina and Dono, 1930).
(9) (Rascanu, 1930-1931a).
(10) (Rascanu, 1931-1932b).
(11) (Rascanu, 1930-1931b).
(12) (Rascanu, 1932-1933).
(13)((Rascanu, 1930-1931c).

All references to the work of A. Rascanu are from Gmelin, System No. 55, pg. 135-136.

and $NH_4UO_2Cl_4 \cdot 2H_2O$ were first prepared by dissolving $K_2U_2O_7$ or $(NH_4)_2U_2O_7$ in concentrated hydrochloric acid, followed by evaporation until crystallization occurred (Peligot, 1842a). Crystallization of a uranyl chloride solution containing the desired alkali halide also is effective. With M = potassium, it is necessary either to use an excess of uranyl chloride or to work in concentrated hydrochloric acid solutions, to prevent precipitation of potassium chloride. Thus, $\underline{K_2UO_2Cl_4 \cdot 2H_2O}$ was prepared by E. Rimbach (1904) by crystallizing an aqueous solution containing equi molecular quantities of the components, together with at least 15 per cent hydrochloric acid. $K_2UO_2Cl_4 \cdot 2H_2O$ forms yellow, triclinic crystals with a:b:c = 0.607:1:0.560, $\alpha = 80^\circ41'$, $\beta = 77^\circ42'$, and $\gamma = 91^\circ18'$. It is very soluble in water. Below 60°C dissolution occurs with decomposition, and the undissolved residue is mostly potassium chloride; above 60°C the solute and the undissolved solid have the same composition. The heat of dissolution is about 2 kcal/mole at 18°C, in infinitely dilute solution (1 mole in 2500 moles)(Aloy, 1896). The compound can be dehydrated at 100°C, but only with some decomposition. At red heat it melts with evolution of chlorine. Hydrogen reduces it. In contradistinction to $K_3UO_2F_5$, the compound $K_2UO_2Cl_4 \cdot 2H_2O$ is not reduced in sunlight by formic or oxalic acid solution:(Bolton, 1886).

$\underline{Rb_2UO_2Cl_4 \cdot 2H_2O \text{ and } Cs_2UO_2Cl_4}$ are prepared similarly to $K_2UO_2Cl_4$ (Rimbach, 1904). The rubidium compound is isomorphous with the potassium and ammonium salts. The rubidium and cesium salts dissolve in water without decomposition. They are thus more stable than the complex with potassium chloride,(and also that with NH_4Cl, cf. below), both of which dissociate upon dissolution at room temperature. A certain correlation appears to exist between stability of the complex and the size of the cation; the larger the latter, the stronger the complex. The cesium compound crystallizes in anhydrous form; the rubidium compound has been observed to do so occasionally. According to Wells and Boltwood (1895) (who first studied these compounds), the cesium compound forms shiny rhombic crystals; but Nichols and Howe (1919) report the substance to be triclinic. The potassium, cesium, and ammonium salts have recently been grown as large crystals, and their absorption and fluorescence spectra studied; details will be discussed elsewhere (SAM-Columbia 5)(Chapter).

Quaternary ammonium salts form an analogous series of compounds. These differ from the complexes discussed in section 3.4 h in that the ligand is a <u>salt</u>, rather than a free base. Rimbach (1904) has described compounds derived from ammonium chloride, trimethylammonium chloride, tetramethylammonium chloride, and tetraethylammonium chloride; attempts to prepare hydroxylamine and hydrazine derivatives were unsuccessful. <u>Ammonium uranyl chloride</u>, $(NH_4)_2UO_2Cl_4 \cdot 2H_2O$, can be prepared from a concentrated hydrochloric acid solution of uranyl chloride and ammonium chloride. It forms very unstable crystals which are isomorphic with the potassium compound. It dissolves in water with decomposition below 70°C. <u>Mono, di</u>, and <u>trimethylamine hydrochlorides</u> form unstable compounds of the type $[(CH_3)_3N]_2UO_2Cl_4$. Tetramethylammonium uranyl chloride, $[(CH_3)_4N]_2UO_2Cl_4$, can be prepared from an aqueous solution of the components as greenish-yellow, strongly fluorescent, tetragonal crystals (a:c = 1:0.9057) which dissolve without decomposition in water. <u>Tetraethylammonium uranyl chloride</u> $[(C_2H_5)_4N]_2UO_2Cl_4$ is likewise prepared by slow crystallization from an aqueous solution containing equivalent proportions of the components. If forms yellow tetragonal crystals, a:c = 1:0.9094, isomorphic with the corresponding tetra methyl compound; like the latter, it dissolves in water without decomposition. Ethylene diammonium uranyl chloride (Grossman and Schuck, 1906), $C_2H_4(NH_3)_2UO_2Cl_4$, best prepared by addition of excess hydrochloric acid to a water solution of ethylenediamine and then addition of an equimolar amount of uranyl chloride, forms very hygroscopic, yellow, prismatic crystals which melt at 219°C (not sharp). The compounds: pyridinium uranyl chloride $(C_5H_6N)_2UO_2Cl_4$ yellow crystalline powder, soluble in water and alcohol) (Kalischer, 1902), β - lutidinium uranyl chloride $(C_7H_{10}N)_2UO_2Cl_4$ (Williams, 1881), and quinolinium uranyl chloride $(C_9H_8N)_2UO_2Cl_4$) (Williams, 1856), have also been prepared. The analogous oxonium salt, xanthylium uranyl chloride $(C_{13}H_9O)_2UO_2Cl_4$ (Fosse and L. Lesage, 1906), is also known.

4. Uranium (IV) Oxychloride, $UOCl_2$

Several reports appear in the older literature purporting to describe this substance. A. Benrath (1917) claimed that anhydrous uranium oxychloride resulted from photochemical reduction of an ether solution of uranyl chloride in direct sunlight. The product was described as light green in color. Reduction in alcohol-ether mixtures gave complex mixtures of basic salts; in aqueous solution, only hydrated uranium dioxide formed. Little reliance can be placed on these results; no experimental details were given, and the description of the product evokes doubt as to their correct identification.

Aloy found that evaporation of a uranium tetrachloride solution at low temperatures in vacuum yielded an amorphous precipitate re-dissolution

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of this precipitate in ethanol and re-precipitation by ether, gives a product which, after thorough washing with ether and drying in a desiccator, has the composition $UOCl_2 \cdot 0.5\ H_2O$. It is described as a bright green, crystalline substance, rather soluble in water; such solutions decompose on heating with separation of hydrated uranium dioxide. These findings are confirmed by observations at UCRL that an aqueous solution of uranium tetrachloride, when dried at 100°C in air, or at 120°C in dry hydrogen chloride, gives solids with the composition $UO_{1.1}Cl_{1.9} \cdot 1.2\ H_2O$ and $UOCl_{2.02} \cdot 1.25\ H_2O$ (UCRL 4). (See also Chapter XIV)

The most direct and generally satisfactory synthesis of uranium oxychloride consists in dissolving UO_2 in excess molten UCl_4 (600°C) (Brown 1,5). The equilibrium:

$$(19) \qquad UO_2 + UCl_4 \rightleftharpoons 2UOCl_2$$

is established under these conditions. After cooling and grinding, the excess UCl_4 can be removed at 450°C in vacuum, conditions under which disproportionation of the uranium oxychloride is negligible.

Uranium oxychloride has also been prepared at the UCRL (cf UCRL 4) by treating UO_2 with UCl_4 vapors. The uranium oxychloride obtained in this way is not as pure as that prepared by liquid phase reaction.

At Ames two unsuccessful attempts were made to prepare uranium(IV) oxychloride. In one, chlorine was reacted with $U_3O_2S_4$, (in analogy to a reaction successfully used in the preparation of uranium oxybromide) but the product was only a mixture of uranyl chloride with higher uranium chlorides. In the second attempt, superheated water vapor was conducted (in a stream of inert gas) over UCl_4, this, too, failed to produce $UOCl_2$ of satisfactory purity (MP Ames 5).

Uranium oxychloride has been described by the Ames Group as yellow feather-shaped crystals, but were called green by workers at Brown University. The yellow crystals are stable in air and dissolve in water to form a green solution. Preliminary x-ray data at Ames (MP Ames 7) on single crystals have been obtained. They appeared to be tetragonal or hexagonal. The spacing along the needle axis is 3.32A, as derived from layer line spacings. The layer line spacings normal to the needle axis are about 40A but are indistinct. Some preliminary x-ray work has also been done elsewhere, but no conclusions as to the structure are as yet available (John Hopkins 1). A value of 2.4 has been reported for the dielectric constant of solid uranium oxychloride (CEW-TEC 3).

Heat of Formation of Uranium(IV) Oxychloride (UCRL 5). The heat of solution of uranium(IV) oxychloride has been determined as $\Delta H = -16.7 \pm 0.2$ kcal/mole, from which the heat of formation can be calculated:

$$(20) \quad U_{(s)} + Cl_{2(g)} + \tfrac{1}{2} O_{2(g)} \longrightarrow UOCl_{2(s)}, \quad \Delta H_{298} = -261.7 \text{ kcal/mole}$$

Equilibrium Pressure of Uranium Tetrachloride above Uranium Oxychloride (UCRL 6). As mentioned above, the reaction

$$(21) \quad UO_{2(s)} + UCl_{4(g)} \rightleftharpoons 2UOCl_{2(s)}$$

is reversible. The equilibrium pressure of UCl_4 above uranium (IV) oxychloride has been measured between 460°C and 540°C, and the results are summarized in Table 7. These values yield for the ΔH of reaction (21) a value of 55.1 kcal. The equilibrium decomposition pressure of UCl_4 over uranium(IV) oxychloride at 500°C is approximately one hundred times smaller than the vapor pressure of UCl_4 at the same temperature.

TABLE 7

EQUILIBRIUM PRESSURE OF URANIUM TETRACHLORIDE ABOVE PURE URANIUM OXYCHLORIDE

t°C	$\frac{1}{T} \times 10^3$	Pressure of UCl_4 (mm Hg)
460	1.364	7.1×10^{-4}
470	1.346	1.18×10^{-3}
480	1.328	1.95×10^{-3}
490	1.311	3.13×10^{-3}
500	1.294	5.0×10^{-3}
510	1.277	8.1×10^{-3}
520	1.261	1.28×10^{-2}
530	1.245	1.97×10^{-2}
540	1.230	3.03×10^{-2}

Equilibrium of Reduction of Uranium Oxychloride by Hydrogen. (UCRL 7) Although the products of reduction of uranium oxychloride by hydrogen have not been identified with certainty, UOCl appears to be the most likely product. Consequently, all of the calculations have been referred to the reaction:

$$UOCl_{2(s)} + \tfrac{1}{2}H_{2(g)} \rightleftharpoons UOCl_{(s)} + HCl_{(g)} \qquad (22)$$

The experimental values of the equilibrium constant are given in Table 8. From these data one obtains, $\Delta H_{673°K} = 10.6$ kcal/mole (± 10-15 per cent). $\Delta F^{o}_{673°K}$ is then 6.03 kcal/mole and $\Delta S^{o}_{673°} = 6.79$ e.u.

Thermodynamic Constants (UCRL 8). MacWood has given the following values for the thermodynamic constants of uranium oxychloride:

$\Delta H_{298} = -261.7$ kcal/mole

$\Delta F_{298} = -246.3 \pm 1.5$ kcal/mole

$S_{298} = 38.1$ e.u.

TABLE 8

EQUILIBRIUM CONSTANTS FOR REDUCTION OF URANIUM OXYCHLORIDE BY HYDROGEN

$K = P_{HCl}/P_{H_2}^{\frac{1}{2}}$ (P in atmospheres)

t^oC	T^oK	$\frac{1}{T} \times 10^3$	K
300	573	1.745	<0.004
350	623	1.605	0.0061
385	658	1.520	0.0095
400	673	1.486	0.011
450	723	1.383	0.020

For details of the calculations and the assumptions involved, we refer the reader to McWood's paper.

Chemical Properties. Few of the chemical properties of uranium oxychloride have been studied. Uranium oxychloride reacts with carbon tetrachloride at 170°C to form uranium tetrachloride. Liquid hydrogen fluoride at room temperature gives uranium tetrafluoride and not uranium oxyfluoride.

5. Uranyl Bromide, UO_2Br_2.

Uranyl bromide appears to be distinctly less stable than the fluoride and chloride. The preparation of anhydrous uranyl bromide was first described by Hermann (1861) and later by von Unruh (1909). Bromine vapors were passed over a mixture of uranium dioxide and charcoal at elevated temperatures, producing a mixture of uranium tetrabromide and uranyl bromide.

von Unruh separated the uranyl bromide by dissolving it in a mixture of alcohol and ether. Uranyl bromide etherate, $UO_2Br_2 \cdot 2(C_2H_5)_2O$ can be obtained as hygroscopic, red, fluorescent needles from this solution. Most of the ether is lost in vacuum. Richards and Merigold (1902) treated U_3O_8 with bromine or with hydrogen bromide but observed no reaction. A number of workers have prepared anhydrous uranyl bromide by dehydration of uranyl bromide hydrate. This work will be discussed in Section 5.2.

5.1 Preparation of Anhydrous Uranyl Bromide (MP Ames 8). The Ames group prepared anhydrous uranyl bromide by reaction of oxygen with uranium tetrabromide:

(23) $UBr_4 + O_2 \longrightarrow UO_2Br_2 + Br_2$

The temperature regulation is important. Below 140°C the reaction is extremely slow; at 200°C considerable amounts of U_3O_8 are produced. The best range is 150°-160°C, preparations analyzing 96 per cent uranyl bromide can be readily obtained at this temperature. X-ray photographs showed no UO_2, U_3O_8, UO_3, or UBr_4 to be present in the product.

Uranium tribromide, UBr_3, when treated with oxygen at room temperature, burns vigorously, this is therefore not a good preparative method. It had been observed (MP Ames 9) that uranium dioxide does not react with bromine even at 720°C. Anhydrous hydrogen bromide reacts at 100°C with dry ammonium diuranate, $(NH_4)_2U_2O_7$, to give, among other products, a water-soluble substance thought to be a double salt of ammonium bromide and uranyl bromide.

5.2 Preparation of Hydrated Uranyl Bromide. Richards and Merigold (1902) prepared aqueous solutions of uranyl bromide by the old method of Berthemot (1830), wherein uranium dioxide suspended in water, is heated with bromine. After excess bromine has been removed by evaporation, a solution of uranyl bromide remains which can then be concentrated to a syrup. The yield of crystals from the syrup is small, and it is almost impossible to wash them free of mother-liquor, so great is their solubility in water and in alcohol.

Sendtner (1879) obtained crystals of the hydrate by dissolving hydrated uranium dioxide in aqueous hydrobromic acid. The yellow solution was concentrated to a syrup and then dried in a desiccator. The hygroscopic, unstable crystals so obtained had the composition $UO_2Br_2 \cdot 7H_2O$. Repeated evaporation of uranyl acetate, first with hydrobromic acid and then with water also yields an aqueous solution of uranyl bromide (von Unruh, 1909). Large yellow-green crystals form in a desiccator from this solution. These crystals are soluble in amyl alcohol; water of crystallization forms a separate layer and the alcoholic solution can be decanted. The solution can be dehydrated even more completely by azeotropic distillation. von Unruh suggested the use of ether for dehydration, but Richards and Merigold (1902) had stated that uranyl bromide reacts with ether. It is doubtful whether alcohol-free uranyl bromide can at all be obtained from alcoholic solutions.

5.3 <u>Properties of Uranyl Bromide.</u> Uranyl bromide is a bright red, very hygroscopic solid which turns yellow in the presence of water vapor. It dissolves very readily in water to a yellow solution. Ethanol solutions of uranyl bromide are rather stable; in the presence of moisture and light some reduction to U(IV) occurs (Berkeley 2). Uranyl bromide, as has already been noted, is also soluble in ether and amyl alcohol.

Uranyl bromide hydrate, $UO_2Br_2 \cdot 7H_2O$, decomposes in moist air with evolution of hydrogen bromide and formation of hydrated uranium oxide.

The compound is very soluble in water and exhibits reactions characteristic of UO_2^{++} ions. Aqueous solutions undergo extensive hydrolysis on boiling (de Coninck, 1902).

Uranyl bromide is thermally unstable as decomposition with slow liberation of bromine occurs even at room temperature; bromine is more rapidly evolved in a helium atmosphere at 250°C. However, even at 350°C, 48 hours are required before complete decomposition. Since the reverse reaction does not take place even at 720°C, the decomposition is irreversible and its rate depends only on temperature and not on the partial volume of bromine (MP Ames 10). Ignition of $UO_2Br_2 \cdot 7H_2O$ in air leads eventually to formation of uranium dioxide, accompanied by evolution of bromine and hydrogen bromide. The uranium dioxide is red and appears to present one more of the many different varieties of this oxide (see Chapter XI, p).

Uranyl bromide, like the fluoride and chloride, readily forms double salts. The ammoniates, $UO_2Br_2 \cdot 2NH_3$, $UO_2Br_2 \cdot 3NH_3$, and $UO_2Br_2 \cdot 4NH_3$, can be prepared by treatment of ethereal or ethanolic solutions of uranyl bromide with ammonia (von Unruh, 1909). $UO_2Br_2 \cdot 4NH_3$, a deeply colored orange-red compound made by treating the diammoniate with liquid ammonia, decomposes rapidly at room temperature.

Compounds of the type $M_2UO_2Br_2 \cdot 2H_2O$ have also been prepared (Sendtner, 1879). Ammonium or potassium diuranates dissolved in hydrobromic acid and evaporated to crystallization on a water-bath, form $\underline{(NH_4)_2UO_2Br_4 \cdot 8H_2O)}$, or $\underline{K_2UO_2Br_4 \cdot 2H_2O}$ - large rhombic, yellow crystals, very soluble in water. These salts form only if a large excess of acid is used. If the pure salt is dissolved in water, it cannot be regenerated. Ignition of the potassium complex leads to a mixture of uranium dioxide and potassium salts. The uranyl bromide double salts are more unstable than the corresponding chlorine compounds. The pyridine compound, $(C_5H_6N)_2UO_2Br_4$, has been prepared by addition of pyridine to a boiling solution of uranium trioxide in excess alcoholic hydrobromic acid. On cooling, yellow crystals of the complex are formed (Loebel, 1907).

Uranyl bromide forms a series of addition compounds with various basic organic compounds. An etherate, $UO_2Br_2 \cdot 2(C_2H_5)_2O$, has been described by von Unruh (1909). It is a yellow-green, fluorescent, crystalline substance, very hygroscopic, which decomposes rapidly in air with evolution of bromine. R. Ráscanu (1930--1931d; 1930--1931 a,b; 1932--1933) has examined a series of addition compounds of uranyl bromide with organic nitrogen bases. These are prepared exactly as the very similar uranyl chloride derivatives (cf section 3.3). The solubilities of the uranyl bromide complexes differ from those of the uranyl chloride compound; they are given in Table 9.

The xanthylium compound, $UO_2Br_2 \cdot 2C_{13}H_9OBr$ (yellow crystals), has also been prepared (Fosse and Lesage, 1906).

6. Uranium (IV) Oxybromide, $UOBr_2$

The preparation of this compound was prompted by the observation (MP Ames 9) that a yellow residue was frequently observed on sublimation of uranium tetrabromide. Its analysis indicated it to be uranium oxybromide. A method of preparation based on the following reactions has been developed at Ames (MP Ames 11):

(24) $3UO_2 + 2CS_2 \xrightarrow{900^\circ C} U_3O_2S_4 + 2CO_2$

(25) $U_3O_2S_4 + 6Br_2 \xrightarrow{600^\circ C} 2UOBr_2 + UBr_4 + 2S_2Br_2$

TABLE 9

COMPLEX COMPOUNDS OF URANYL BROMIDE WITH ORGANIC BASES

Organic Base	Complex	Description	Solubility
p-nitrosodimethyl aniline	$UO_2Br_2 \cdot 2(CH_3)_2NC_6H_4NO$	Stable in air. Brick-red powder	Slightly sol. in water. Insol. in alc., ether, acetone and chloroform.
p-nitroso diethyl aniline	$UO_2Br_2 2(C_2H_5)_2NC_6H_4NO$	Dark brick-red powder	Same as above
Methyl acetanilide	$UO_2Br_2 \cdot 2C_6H_5N(CH_3)(C_2H_3O)$	Stable in air. Shiny, yellow crystals.	Sol. in water and alc. Insol. in ether.
Acet-p-phenetidine	$UO_2Br_2 \cdot 4C_{10}H_{13}O_2N$	Orange yellow; stable in air.	Insol. in water, dif. sol. in alc., acetone, and chloroform. Insol. in ether and amyl alc. Completely sol. in amyl alcohol on heating.
Antipyrine	$UO_2Br_2 \cdot 2C_{11}H_{12}N_2O$	Stable in air.	Sol. in water, slightly sol. in alc. Insol. in ether and chloroform.
Bromantipyrine	$UO_2Br_2 \cdot 2C_{11}H_{11}BrN_2O$	Yellow needles.	Sol. in warm H_2O or alc., slightly sol. in boiling acetone. Insol. in ether or $CHCl_3$. Sol. in HCl.

Bromine vapor, carried in a stream of nitrogen, is passed over $U_3O_2S_4$ at 600°C until distillation of UBr_4 and S_2Br_2 ceases. The nonvolatile uranium oxybromide is a greenish-yellow to yellow powder. Analysis shows it to correspond very closely to the composition $UOBr_2$, and x-ray studies show it to be a pure phase, and not a mechanical mixture of uranium dioxide and uranium tetrabromide.

Uranium (IV) oxybromide is not particularly hygroscopic, but it dissolves readily in water to give a green solution. The solution is stable for several hours, after which a black precipitate, presumably hydrated uranium dioxide, begins to precipitate. This precipitate is similar to that obtained when aqueous solutions of uranium tetrabromide are treated with a base. It has been suggested by the Ames workers (MP Ames 12) that stable UO^{++} ions exist in solutions of uranium oxybromide; this interpretation is supported by the fact that electrometric titration shows that four equivalents of hydroxide are required for precipitation per mol of uranium tetrabromide and only two per mole of $UOBr_2$. This point is discussed at greater length in Chapter XVI.

Uranium (IV) oxybromide appears to be stable and nonvolatile at 600°C in an inert atmosphere; at 800°C, however, disproportionation to uranium dioxide and uranium tetrabromide occurs. U_3O_8 forms on ignition in air.

6.1 Hydrogen Reduction Equilibrium of Uranium Oxybromide (UCRL 9). The equilibrium of uranium oxybromide reduction by hydrogen has been studied between 300°C and 400°C. Reduction proceeds with the formation of hydrogen bromide; the analysis of the data is made on the assumption that UOBr is the other product:

(26) $UOBr_{2(s)} + \frac{1}{2}H_{2(g)} \longrightarrow UOBr_{(s)} + HBr_{(g)}$

The experimental equilibrium constants are given in Table 10.

TABLE 10

EQUILIBRIUM CONSTANTS FOR REDUCTION OF URANIUM OXYBROMIDE BY HYDROGEN

$K = P_{HBr} / P_{H_2}^{\frac{1}{2}}$ (P in atmospheres)

$t^{\circ}C$	$T^{\circ}K$	$\frac{1}{T} \times 10^3$	K
300	573	1.745	<0.004
350	623	1.605	0.0061
375	648	1.543	0.0078
400	673	1.486	0.0108
425	698	1.433	0.0139
440	713	1.403	0.0162

From the above data, one calculates $\Delta H_{673^{\circ}K} = 10.1$ kcal, $\Delta F^{o}_{673^{\circ}K} = 6.06$ kcal/mole, and $\Delta S_{673^{\circ}K} = 6.01$ e.u., for reaction (26).

Thermodynamic Constants (UCRL 8). The following thermodynamic constants have been given by MacWood for uranium oxybromide:

$\Delta H_{298} = -246.9 \pm 0.7$ kcal/mole

$\Delta F_{298} = -231.3 \pm 2.0$ kcal/mole

$S_{298} = 42.9$ e.u. (estimated)

The above heat of formation is based on a calorimetric determination of of the heat of solution of uranium oxybromide, which gave $\Delta H = -16.3 \pm 0.2$ kcal/mole (UCRL 5).

7. Uranyl Iodide, UO_2I_2

It is doubtful whether pure uranyl iodide has ever been prepared in the solid state. From what little is known about this substance, it appears likely that it is considerably less stable than uranyl bromide which already has a distinct tendency to lose its halogen. Various workers have attempted to prepare uranyl iodide by reaction of iodine vapors or hydrogen iodide vapors or hydrogen iodide with a mixture of uranyl dioxide and carbon, but without success (von Unruh, 1909).

Aqueous solutions of uranyl iodide may be readily prepared, however. von Unruh (1909) prepared such solutions by treating uranyl acetate with hydroiodic acid. Concentration of such a solution by heating results in extensive decomposition. Drying in vacuum yields yellow-green fluorescent needles which decompose rapidly in air with liberation of iodine. The substance was not analyzed. Previous attempts by Sendtner (1879) to concentrate solutions of $UO_3 \cdot H_2O$ in hydroiodic acid resulted in every case in the evolution of large amounts of iodine (Sendtner, 1879); and a product heavily contaminated with free iodine was obtained. It appears unlikely that aqueous solutions of uranyl iodide can be dehydrated without extensive decomposition.

Solutions of uranyl iodide in water or organic solvents can be readily prepared by double decomposition reactions. The reactants are so chosen that one of the products is uranyl iodide and the other a salt insoluble in the solvent used. J. Aloy (1901a) dissolved partially dehydrated uranyl nitrate hexahydrate in ether and added a slight excess of barium iodide. On removing the insoluble barium nitrate and concentrating the red solution in vacuum, an unstable, red, very deliquescent, crystalline material was obtained. A methanolic solution of uranyl nitrate treated with sodium iodide yields a solution of uranyl iodide. von Unruh prepared non-aqueous solutions of uranyl iodide by dissolving in ether, the solid material, obtained by evaporation of an aqueous solution, and then using calcium chloride and sodium metal to remove water and free iodine. Crystals, contaminated with iodine, and presumed to be $UO_2I_2 \cdot 2(C_2H_5)_2O$ can be obtained from the ethereal solution, by evaporation in vacuum or in a stream of dry air. Double decomposition has also been used for preparing aqueous solutions. Thus, a solution of uranyl sulfate may be treated with the equivalent amount of barium or calcium iodide (Truttwin, 1925).

It has been reported that uranyl iodide is soluble in methyl acetate, ethyl acetate, acetone, and pyridine, (Naumann, 1904,1909), as well as in water, ether, and methyl, ethyl, or amyl alcohols.

Uranyl iodide forms a series of addition compounds with ammonia (von Unruh, 1909). Uranyl iodide in ether or amyl alcohol solution gives, with gaseous ammonia, $\underline{UO_2I_2 \cdot 2NH_3}$ more prolonged treatment with ammonia gives $UO_2I_2 \cdot 3NH_3$ as a golden-yellow amorphous solid. Treatment of the diammoniate with liquid ammonia at 0°C gives the very unstable $UO_2I_2 \cdot 4NH_3$ which decomposes rapidly above 5°C.

Aqueous or ethanolic solutions of uranyl iodide have been alleged to possess the property, of dissolving normally insoluble heavy metal iodides such as bismuth iodide, BiI_3, or mercuric iodide, HgI_2. Compounds such as UO_2BiI_5 can be isolated from these solutions (Truttwin, 1925).

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